# CRYSTALLOGRAPHIC CALCULATIONS ON THE SILLIAC ELECTRONIC DIGITAL COMPUTER

## II. STRUCTURE FACTORS

By H. C. FREEMAN*

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*Summary*

Two programmes for crystal structure-factor calculations on the SILLIAC computer are briefly described, with special reference to the problem of coding such computations efficiently for a computer of high speed but limited storage capacity.

## I. INTRODUCTION

Several electronic digital computer programmes for crystal structure-factor calculations have already been described in some detail, either for their own sakes (e.g. Ahmed and Cruickshank 1953 ; Fowweather 1955) or as part of automatic refinement programmes (e.g. Thompson *et al.* 1954 ; Friedlander, Love, and Sayre 1955 ; Lavine and Rollett 1956 ; Sparks *et al.* 1956). In many other laboratories similar routines have been developed (e.g. Jeffrey *et al.* 1957) without the technical details being published. The present paper is therefore intended to be no more than a record of some features of the SILLIAC crystal structure-factor programmes which have been influenced by the particular characteristics of the machine.

Those technical details of SILLIAC which are of direct interest to a programmer—order-types, operation-times, size of store, speeds of in- and output—were summarized in Part I of this series (Freeman 1957). It was emphasized there that for the development of programmes for crystallographic calculations SILLIAC's great attraction was its high speed, while the greatest problem was in the limitations of a store of 1024 40-bit words.

Consideration of these two features as well as of local computing needs influenced the decision to write programmes for crystal structure refinement which would be applicable to selected classes of space groups rather than be completely general. This decision has been justified by the comparatively high speed with which these specialized programmes compute structure factors. Further experience with the computer has shown that a completely general structure-factor routine capable of dealing efficiently with large asymmetric units can be coded only when the size of the SILLIAC memory has been increased.

Accordingly, the existing SILLIAC structure-factor programmes are suitable for crystals belonging, respectively, to : (i) the monoclinic space groups of class $2/m-C_{2h}$, and (ii) the orthorhombic space groups of classes $222-D_2$, $mm2-D_{2h}$, and $mmm-C_{2v}$ (with the exception of the space groups $Fddd-D_{2h}^{24}$ and $Fdd2-C_{2v}^{19}$).

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The expressions evaluated by these programmes are, respectively,

$$F_{hkl}=4\sum_{j=1}^{N/4} f_j T_f \cos 2\pi(hx_j+lz_j).\cos 2\pi ky_j$$

or

$$=-4\sum_{j=1}^{N/4} f_j T_f \sin 2\pi(hx_j+lz_j).\sin 2\pi ky_j\ ; \qquad \ldots\ldots\ldots \quad (1)$$

and

$$\begin{aligned} F_{hkl}&=[A_{hkl}^2+B_{hkl}^2]^{\frac{1}{2}},\\ \cos\alpha_{hkl}&=A_{hkl}/F_{hkl},\\ \sin\alpha_{hkl}&=B_{hkl}/F_{hkl}, \end{aligned} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

where $A_{hkl}$ and $B_{hkl}$ have the form

$$\pm 2^m \sum_{j=1}^{N/2^m} f_j T_j \begin{pmatrix}\cos\\ or\\ \sin\end{pmatrix} 2\pi hx_j.\begin{pmatrix}\cos\\ or\\ \sin\end{pmatrix} 2\pi ky_j.\begin{pmatrix}\cos\\ or\\ \sin\end{pmatrix} 2\pi lz_j.$$

In these expressions $x_j$, $y_j$, $z_j$ are the coordinates of the $j$th atom expressed as fractions of the unit-cell edges; $f_j$ is the atomic scattering factor of the $j$th atom; $T_f$ is an overall isotropic temperature factor, $\exp(-B\sin^2\theta/\lambda^2)$, (though in the orthorhombic case a separate $B$ may be specified for each atom-*type*); $2^m$ is a multiplicity term, with $m=2$, 3, or 4; and $N$ is the number of atoms in the unit cell.

Each programme can deal with an asymmetric unit of up to 30 atoms of not more than six different kinds. All the $F_{hkl}$'s (and, for the monoclinic case, all the $F_{hkl}$'s) for which $\sin\theta_{hkl}/2\lambda\leqslant 1/2\lambda$ are calculated. The indices are increased in the order $l$, $h$, $k$, for the monoclinic space-groups, and in the order $l$, $k$, $h$ for the orthorhombic ones. The outputs consist, respectively, of: (i) $h$, $k$ for a group of $F$'s; $l$ and $F_{hkl}$ for each reflection; and (ii) $h$, $k$ for a group of $F$'s; $l$ and any or all of $A_{hkl}$, $B_{hkl}$, $F_{hkl}$, $\cos\alpha_{hkl}$, $\sin\alpha_{hkl}$ for each reflection.

## II. Outline of Computation

The quantities which must remain stored for the duration of a calculation are the atomic coordinates, the parameters specifying to which atom-type each atom belongs, the thermal parameters, atomic scattering factor data, and the unit-cell constants. There are other quantities whose values change during the course of the calculation but for whose "current" values storage is required: $h$, $k$, $l$; the $hx_j$, $ky_j$, and $lz_j$, and their trigonometrical functions. For 30 atoms, the monoclinic structure-factor programme requires the use of 320 storage locations (one-third of the memory). In the orthorhombic programme, the number of quantities to be stored is increased to 470, since a considerable gain in computing speed results from the retention of intermediate products of those trigonometrical functions whose arguments do not involve the most rapidly changing index. In order that the programme in this case may be fitted into the store at all it is necessary to "pack" some of the stored numbers two to a storage-location. Whenever one of the numbers is subsequently used or modified,

two or three orders suffice to select the appropriate half of the " word " without disturbing the other half. In arithmetical operations on the fraction represented by the 20 most significant binary digits, the whole word can be used without modification, since the 20 least significant bits—though spurious—will be below the level of significance.

For each reflection, $\sin\theta/2\lambda$ is evaluated and tested to see whether the reflection lies in the observable range. If it does, the new arguments are formed by addition. The indices $h$, $k$, and $l$ are now tested to determine which trigonometrical products are going to be needed. The orders which will select the functions to be multiplied are picked up from a list and are planted further along the programme. At the same time, an obvious economy is achieved by short-circuiting the calculation of unnecessary functions when only the cosines *or* sines are required. These functions are obtained via a standard library subroutine using an economized power series.

It would be absolutely impossible to accommodate in the SILLIAC store complete tables of the atomic scattering factors—whether they be tables of $f$ versus $\sin\theta$ (e.g. Sparks *et al.* 1956 : 100–150 values per atomic species) or $f$ versus $\sin^2\theta$ (e.g. Lavine and Rollett 1956 : 100 values per species ; Rollett, personal communication 1957 : 48 values per species). It has fortunately been found possible to represent the scattering curves within the $CuK_\alpha$ range by sixth-degree polynomials in $\sin\theta/2\lambda$, so that seven locations hold all the coefficients necessary to specify one atom-type. The calculation of these coefficients will be described in a subsequent paper.

## III. Data Coding

When these programmes were written it was expected that many of their users would be located far from the computer and would have to submit their data by correspondence. Much attention was therefore devoted to the design of the input routines, which permit the presentation of data to the computing laboratory in the least complicated form possible, yet ready for immediate punching and processing. In particular :

(i) The data-tapes contain no " directives " (addresses to locate groups of data in the store) and only a minimum number of code symbols. The only symbol which is used is the sexadecimal digit $N$ (=12), and this always marks the end of a group of data of the same type (e.g. the *last* $x_j$ is followed by $N$).

(ii) All quantities are punched as pure integers or fractions, decimal points and zeros preceding them being omitted.

(iii) Programme control is achieved entirely by parameters supplied as part of the data, and these parameters are all specified as signed integers. " Is $\cos\alpha_{hkl}$ to be punched ? Put $+0$ for " *no* " and $+1$ for " *yes* "." Each parameter is examined immediately after being input ; as a result, appropriate orders are chosen from a list already in the store and are planted at the relevant points in the programme. (There

is one exception to this method of programme control: the calculations may be limited to any one of the zero layers by means of one to three modifying orders—coded as orders—written at the end of the data.)

(iv) There are eight possible combinations of the indices: *all* even; $h$ even, $k$ even, $l$ odd; etc. For each of these possibilities, the form of the structure-factor expression is specified by a numerical parameter. The complete list consists of eight signed integers, selected according to the space group. In the monoclinic case, there are only two possibilities in addition to a "no calculation" contingency; in the orthorhombic case, $A_{hkl}$ and $B_{hkl}$ may each assume one or none of 16 forms. When the list of parameters is read the immediate machine action is to modify the subroutine which later tests the $h, k, l$ of each reflection so that each condition will lead to the formation of the desired trigonometrical product.

(v) Data presentation forms have been prepared with the few essential $N$-symbols preprinted and with the required information listed in the correct sequence. The data are punched directly from these forms.

## IV. Computing Times

Some typical computing times, excluding approximately one minute for programme- and data-input, are shown in Table 1.

Table 1

SOME TYPICAL COMPUTING TIMES

| Programme | No. of Atoms | No. of Kinds of Atoms | No. of Type $F$'s | Total Time (min) | Approx. Time per $F$ per Atom (sec) |
|---|---|---|---|---|---|
| Monoclinic .. .. | 8 | 4 | 1200 *hkl* | 11 | 0·07 |
| | 11 | 5 | 400 *hkl* | 5 | 0·07 |
| | 26 | 4 | 300 *h0l* | 4 | 0·03 |
| | 18 | 2 | 200 *h0l* | 3 | 0·05 |
| Orthorhombic .. | 9 | 5 | 832 *hkl* | 7 | 0·06* |
| | 9 | 5 | 832 *hkl* | 13 | 0·10† |

* Output: $h, k, l, A_{hkl}$.
† Output: $h, k, l, A_{hkl}, B_{hkl}, F_{hkl}, \cos\alpha_{hkl}, \sin\alpha_{hkl}$.

## V. Least-Squares Refinement

A programme for the automatic least-squares refinement of structures in the class $2/m$—$C_{2h}$ has been coded. It contains a modified version of the monoclinic structure-factor routine. This programme is organized on lines

similar to those of the ElectroData code described by Lavine and Rollett (1956). The SILLIAC code differs from the latter essentially as follows:

(i) It makes allowance for only one overall two-parameter anisotropic temperature factor;

(ii) the observed $F_{hkl}$'s (Lavine and Rollett's "planes-tapes") can never be stored in SILLIAC: they are read and processed one by one, and the tape is reinserted for each refinement cycle;

(iii) the observed structure factors are listed in increasing order of the indices without segregation of odd and even indices and without signals showing the expression to be used for $F_{hkl}$. The machine finds $hkl$ by counting, and tests the indices to determine the expression appropriate for each reflection. There is, however, provision for the tagging of unobserved or systematically absent reflections.

For an asymmetric unit of 8 atoms of 4 types, one refinement cycle with respect to 585 values of $F_{hkl}$ takes 15 min if the full list of $F_{\text{obs.}}$, $F_{\text{calc.}}$, and $F_{\text{obs.}}-F_{\text{calc.}}$ is punched, and 10·5 min if only the parameter changes, new parameters, $\Sigma\,|F_{\text{obs.}}|$, $\Sigma\,|F_{\text{calc.}}|$, $\Sigma\,|F_{\text{obs.}}-F_{\text{calc.}}|$, $R$-factor, and $\Sigma w(\Delta F)^2$ are output.

## VI. Two-Dimensional Fourier Programme: Addendum

The SILLIAC code for 2-dimensional Fourier summations (cf. Part I of this series, Freeman 1957) has been amended to permit the storage of 1280 (instead of 550) $F_{hk}$'s in four (instead of two) tables. Summation can now be carried out at 1/64's or 1/128's of each of the unit-cell edges. The input routine has been rewritten so that all parameters and instructions are coded as signed integers and then interpreted. The speed of the code has not been significantly reduced by these changes.

## VII. Acknowledgments

The author is grateful for the help of the Director and staff of the Adolph Basser Computing Laboratory, University of Sydney, and for many discussions with Dr. J. M. Bennett.

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# A POLAROGRAPHIC STUDY OF SOME WURSTER SALTS

By J. A. Friend* and N. K. Roberts*

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*Summary*

Four related Wurster salts are subjected to a polarographic investigation. In the case of Wurster's blue, results from the dropping mercury electrode, stationary platinum electrode, and rotated platinum electrode are compared.

The Wurster salt of *p*-phenylenediamine is unstable in aqueous solution but is fairly stable in a mixture of methanol, acetic acid, and water and the decrease of diffusion current with time indicates a disproportionation.

Wurster's red is also unstable in aqueous solution. In the solvent methanol, acetic acid, and water, a wave is observed with the stationary platinum electrode whose $E_{\frac{1}{2}}$ compares favourably with the potentiometric $E'_0$.

Evidence from the three types of electrodes mentioned previously indicates two one-electron waves for Wurster's blue. The semiquinone formation constant qualitatively appears much greater than that reported from potentiometric work. Decrease of diffusion current with time is perhaps due to a disproportionation (the very unstable di-imine has been shown to revert to the radical in aqueous solution).

Polarographic waves given by the Wurster salt of diaminodurene suggest that the radical does not exist in aqueous solution. Waves corresponding to the original amine and duroquinone (formed by hydrolysis of the di-imine) are obtained.

## I. Introduction

The Wurster salts, or univalent oxidation products of *p*-phenylenediamine and its *N*-substituted derivatives, have been the subject of detailed physicochemical studies along certain lines. Michaelis and his collaborators (Michaelis, Schubert, and Granick 1939; Michaelis and Granick 1943) showed by potentiometric and magnetochemical studies that the salts exist in solution as free radicals and in the solid state either as polymers or (in a few cases) as the monomeric free radical.

The free radicals are analogous to the semiquinone ions which exist in the free state in alkaline solutions of some quinones.

The Wurster salt cations are formed in acid solution, and owing to increased resonance are more stable than the uncharged forms. The pH of optimum stability is approximately 4·6. The ions formed have formulae analogous to

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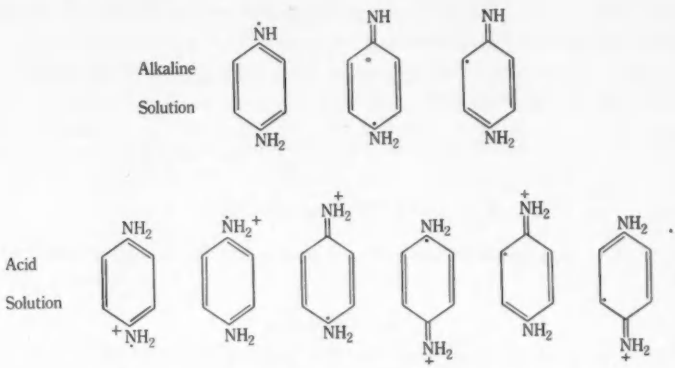



A polarographic study of the oxidation of some *p*-phenylenediamine derivatives was made some years ago by Julian and Ruby (1950). The stationary platinum microelectrode was used. In the present work, as far as possible, the dropping mercury electrode was used, and attention was directed especially to four Wurster salts, the stability of which Michaelis had shown to vary between wide limits.

## II. Experimental

### (*a*) *Materials*

The univalent oxidation products of four amines were studied. Oxidation was carried out with bromine water following Michaelis and Granick (1943) and the Wurster salts were usually isolated as the perchlorate by adding excess $NaClO_4$ to a cold solution. The perchlorate ion is polarographically inert.

(i) p-*Phenylenediamine.*—A few preliminary experiments were carried out with this substance. A technical grade (B.D.H.) was used. The Wurster salt was used in the form of the bromide, but as reported below, was too unstable to be of much value in the present work.

(ii) NN-*Dimethyl*-p-*phenylenediamine.*—This was prepared from dimethylaniline according to the method described by Gattermann (1948). The amine was purified by redistillation and boiled over a range of 1 °C. The Wurster salt was prepared as the perchlorate from the amine dihydrochloride.

(iii) NNN′N′-*Tetramethyl*-p-*phenylenediamine.*—This material was obtained in the form of the dihydrochloride by recrystallization of a sample of Eastman-Kodak product. The molar extinction coefficient of the Wurster salt at 5650 A in water was 12,400 which agreed closely with the value (12,470 $\pm$60) found by Albrecht and Simpson (1955). The *sulphate* of tetramethyl-*p*-phenylenediamine was prepared by treating an ethereal solution of the amine with an ethereal solution of $H_2SO_4$. The product had $SO_4$, 53·4 per cent. Calc. for $(CH_3)_2NH.C_6H_4.NH(CH_3)_2(HSO_4)_2$: $SO_4$, 53·3 per cent.

(iv) *Diaminodurene* (*2,3,5,6-Tetramethyl*-p-*phenylenediamine*).—This was prepared as the dihydrochloride from durene (Light and Co.) by the method of

Nef (Nef 1887). The amine dihydrochloride was recrystallized and the Wurster salt prepared as the perchlorate.

All buffer salts and other chemicals used were of analytical reagent grade. The following buffer solutions were used:

| | |
|---|---|
| pH 3·9–5·7 | 1M $CH_3COOH$–1M $CH_3COONa$. |
| pH 6·0–8·0 | 0·5M $Na_2HPO_4$–0·5M $KH_2PO_4$. |
| pH 9·35 | 0·3M $Na_2B_4O_7.10H_2O$. |

Half-wave potentials in acetate and phosphate buffer of the same pH were identical.

### (*b*) *Apparatus*

Two instruments were used for the polarographic studies. One was a Tinsley automatic ink-recording polarograph, which was used primarily to obtain rapidly polarograms in the region of negative potentials. For much of the work a manual instrument of conventional design was used. This enabled mixed anodic-cathodic waves to be more easily recorded, and could be used readily at positive potentials. It also enabled half-wave potentials to be accurately determined. A Pye galvanometer of sensitivity $2·02 \times 10^{-4}$ μA/mm was used to measure the current in this circuit.

A saturated calomel electrode was used as the reference electrode, in conjunction with a potassium nitrate salt bridge prepared according to the directions of Müller (1951), as the chloride ion is oxidized at the positive potentials used in much of the present work. All potentials are quoted relative to the S.C.E. The cell resistance, as measured with an A.C. bridge, was 750 ohms.

The stationary platinum microelectrode used for potentials more positive than +0·2 V (*v.* S.C.E.) consisted of a piece of wire 0·5 mm in diameter and 5 mm in length, sealed into a Pyrex tube bent at right angles and supported horizontally. The potential was increased at a rate of 20 mV/min.

(i) *Rotated Platinum Microelectrode.*—This electrode was similar to electrode "A" described by Laitinen and Kolthoff (1941). A Gallenkamp laboratory stirrer was used to drive the electrode. The rate of rotation was increased until the current passing remained almost constant. In contrast to the polarograms obtained by Laitinen and Kolthoff those of Wurster's blue were found to be reproducible from day to day.

All measurements were carried out in a thermostat controlled at 25·0±0·1 °C, and oxygen was removed from the solutions by bubbling oxygen-free nitrogen through them. The pH of buffer solutions was measured by means of a Leeds and Northrup glass electrode and potentiometer unit. Measurements of absorption spectra were carried out on a Unicam SP 500 spectrophotometer.

Conductance measurements were made using a Cambridge conductivity bridge and deionized water (specific conductance $1 \times 10^{-6}$ ohm $cm^{-1}$) prepared by treating distilled water with "Bio-deminrolit".

## III. Results

### (*a*) *Polarography of the Wurster Salt of* p-*Phenylenediamine*

This salt was not stable in aqueous solutions, but was more stable in a mixture of water, methanol, and glacial acetic acid in the volume ratio of 5 : 4 : 1. The half-wave potential was too positive to be measured. Oxidation of the bromide ion distorted the shape of the wave.

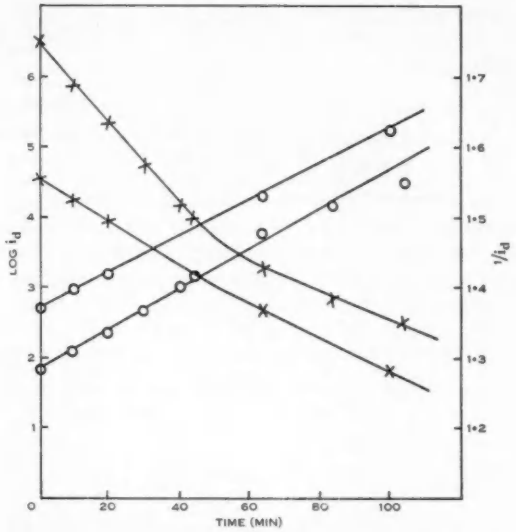
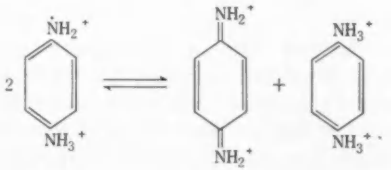



Fig. 1.—Wurster salt from *p*-phenylenediamine. Variation of diffusion current with time, apparent pH 2·56. × Log $i_d$ *v.* $t$ (min) left-hand ordinate. ○ $1/i_d$ *v.* $t$ (min) right-hand ordinate.

By studying the rate of decay of the radical, measured by the rate of decrease of the cathodic diffusion current, it was concluded that the decomposition was second-order as the plot of $1/i_d$ against time was linear (Fig. 1). This is perhaps due to a disproportionation




two molecules of the salt giving one molecule each of the diamine and the di-imine, which is very unstable and decomposes immediately.

(*b*) *Wurster Salt of* NN-*Dimethyl*-p-*phenylenediamine* (*Wurster's Red*)

This salt is fairly stable in the water-methanol-acetic acid solvent, apparent pH=2·56 (*v.* glass electrode). Decomposition was accompanied by a colour change from red to blue.

The variations of limiting current with (height of mercury)$^{\frac{1}{2}}$ indicated a diffusion-controlled wave. The half-wave potential $E_{\frac{1}{2}}$ determined with the stationary platinum microelectrode was approximately +0·39 V. The sulphate of the parent amine gave a similar wave at the same potential, which may be compared with the potentiometric $E_0$ value found by Michaelis and Hill (1933) of +0·36 V (pH=2·56).

(*c*) *Wurster Salt of* NNN′N′-*Tetramethyl*-p-*phenylenediamine*

This salt remained unchanged in the solid state. It was studied mainly in acetate buffer at ionic strength of 1·0.

(i) *Dropping Mercury Electrode.*—The polarogram of a fresh solution (prepared by adding a small quantity of salt to buffer solution from which the dissolved oxygen had been removed) consisted of an almost completely cathodic wave. As the solution aged the anodic portion of the wave increased, the total height remaining constant (Fig. 2).

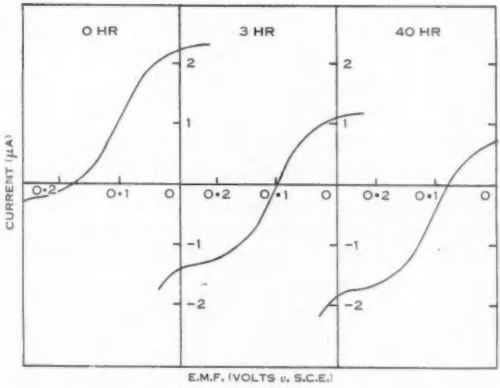



Fig. 2.—Wurster's blue. Change of wave, with time (dropping mercury electrode); pH 5·3.

A solution of the sulphate of the parent amine (the chloride ion is oxidized at the dropping mercury electrode) gave an anodic wave of the same shape and with the same half-wave potential. Equal molar concentrations of radical and amine gave the same wave height. The wave of the amine gradually developed a cathodic portion on standing owing to atmospheric oxidation of the base to the free radical. When a steady state was reached the ratio of the height of the cathodic portion to that of the anodic portion was the same as for the free radical. The half-wave potential of the system remained constant.

The wave obtained was diffusion controlled for the following reasons:

(1) Limiting current was proportional to (height of mercury)$^{\frac{1}{2}}$.
(2) Limiting current was proportional to the concentration (over the range 0·5–3 mM).
(3) Temperature coefficient of the diffusion current was about 2 per cent. near 20 °C.

A graph of $\log i/(i_d-i)$ ($i_d$=diffusion current, $i$=current at potential $E$) as a function of $E$ for the pH range 3·9–9·35 was linear and varied in slope from 60–70 mV/log unit

| pH | Slope (mV) | pH | Slope (mV) |
|---|---|---|---|
| 3·9 | 60 | 6·5 | 63 |
| 4·6 | 60 | 7·2 | 70 |
| 5·3 | 69 | 7·5 | 68 |
| 5·7 | 62 | 8·0 | 64 |
| 6·0 | 60 | 9·35 | 60 |

The system is apparently reversible since the half-wave potential of the wave remained constant as a solution of the radical or amine aged. The slope at pH 5·3, 7·2, and 7·5 is admittedly high for a fully reversible process but normal at the other pH values. An adsorption process may be involved. although no direct evidence of differential adsorption could be detected.

Application of the Ilkovič equation (Ilkovič 1934) confirmed the result obtained from the logarithmic analysis of the wave.

Over the pH range studied the height of the wave remained constant. The main problem in applying the Ilkovič equation was the evaluation of the diffusion coefficient ($D$) of the Wurster cation. An approximate value of $7\times10^{-6}$ cm$^2$ sec$^{-1}$ was indicated by analogy with hydroquinone ($D=7\cdot2\times10^{-6}$ cm$^2$ sec$^{-1}$). Conductance measurements at concentrations of 0·25 and $0\cdot5\times10^{-3}$M yielded a value of the equivalent conductance $\Lambda=108\cdot5$ mhos. Putting this value approximately equal to $\Lambda_0$ the value at infinite dilution, and subtracting the ionic conductance of the perchlorate ion (68 mhos at 25 °C), the ionic conductance of the cation is found to be 40·5 mhos. Applying the Nernst relationship for an ion of valency $z$ (see Kolthoff and Lingane 1941)

$$D^0=\ 2\cdot67\times10^{-7}\lambda^0/z,$$
$$D^0=10\cdot8\times10^{-6}\text{ cm}^2\text{ sec}^{-1}.$$

(The superscripts indicate that the formula is valid at infinite dilution.)

By a similar technique the diffusion coefficient of the amine dihydrochloride was found to be $9\cdot8\times10^{-6}$ cm$^2$ sec$^{-1}$. In making these measurements, excess of free amine was added to reduce the hydrolysis of the hydrochloride. The value is only approximate as the free amine was rapidly oxidized by the air.

A value of $10\cdot0\times10^{-6}$ cm$^2$ sec$^{-1}$ was adopted as an approximate figure for $D$. However, the true value is probably considerably smaller since the concentration of the radical was usually $10^{-3}$M and the base solution had a high ionic strength (1·0).

The Ilkovič equation gives the number of electrons involved in the reduction process independently of any assumption of reversibility, and so provides necessary information for the interpretation of the logarithmic plot. It was used in the form

$$i_d = 605nD^{1/2}cm^{2/3}t^{1/6},$$

where $n$ electrons are involved in the reduction of an ion of diffusion coefficient $D$ at concentration $c$ mM/l using a capillary of drop-time $t$, and a flow-rate of $m$ mg Hg/sec. In the present instance, $i_d = 2 \cdot 3$ μA, $c = 1$ mM, $m^{2/3}t^{1/6} = 1 \cdot 444$ mg$^{2/3}$ sec$^{-1/2}$, $D = 10^{-5}$ cm$^2$ sec$^{-1}$. This gives $n = 0 \cdot 83$.

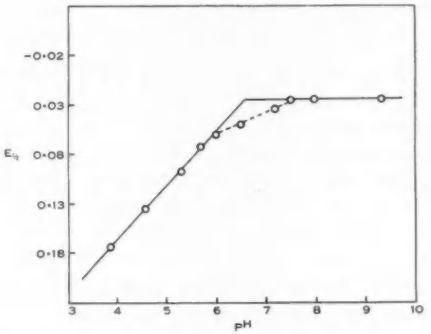



Fig. 3.—Wurster's blue. Half-wave potential *against* pH (dropping mercury electrode).

A graph of the $E_{\frac{1}{2}}$ against pH was linear over the pH range 3·9–6·0, with a slope of 55 mV/pH unit. From pH 6·0–7·5 the slope was 22 mV/pH unit and from pH 7·5–9·35 zero slope (Fig. 3). Acetate buffer was employed from pH 3·9–5·7, phosphate buffer from pH 6·0–8·0, and borate buffer for pH 9·35. This $E_{\frac{1}{2}}$-pH relationship is consistent with a one-electron system.* Interpolation gives pH 6·6 as the dissociation constant of the system. Because the slope becomes flatter at this point, the dissociation must refer to the reduced form.

(ii) *Stationary Platinum Electrode.*—Because only one wave was obtained with the dropping mercury electrode, which was shown to be a one-electron step, a platinum electrode was constructed to investigate the positive potential range inaccessible to the dropping mercury electrode for the presence of an expected anodic one-electron wave.

At the stationary platinum microelectrode, a wave as in (*a*) was observed, but a second wave at a positive potential was found as well (Figs. 4 and 5). The ratio of the heights of the two waves was approximately 1 : 2·5 at all pH's studied. Waves obtained with this electrode were not as reproducible as those

* The range 6·0–7·5 is regarded as a transition range with an average slope of 22 mV/pH unit. It is unlikely that two dissociation constants would be so close.

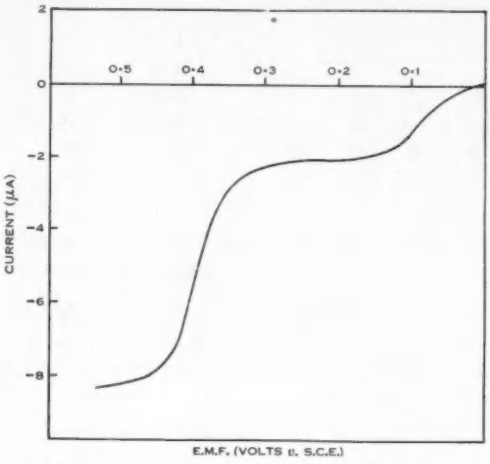



**Fig. 4.**—Parent amine of Wurster's blue. Wave from stationary platinum electrode; pH 5·3.

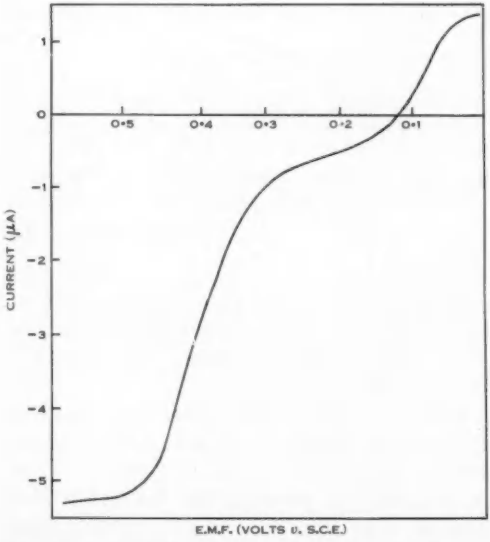



**Fig. 5.**—Wurster's blue. Wave from stationary platinum electrode; pH 5·3.

found at the dropping mercury electrode. A comparison of the half-wave potentials and slopes of the waves obtained at the two electrodes follows:

(1) Small Wave

| | | | |
|---|---|---|---|
| pH .. .. .. .. | 3·9 | 4·6 | 5·3 |
| $E_{\frac{1}{2}}$ (Pt) .. .. .. | 0·17 | 0·13 | 0·09 |
| $E_{\frac{1}{2}}$ (Hg) .. .. .. | 0·175 | 0·136 | 0·098 |
| Slope from log plot (Pt) | 60 | 60 | 69 |
| Slope from log plot (Hg) | 60 | 60 | 69 |

(2) Large Wave

| | | | |
|---|---|---|---|
| $E_{\frac{1}{2}}$ (Pt) .. .. .. | 0·44 | 0·42 | 0·39 |
| Slope from log plot .. | ~60 | ~60 | ~60 |

The large wave had the slope of a one-electron step; however, it is not clear why it was so large. Changing the base electrolyte to a mixture of water, methanol, and glacial acetic acid in the volume ratio 5 : 4 : 1 did not alter the relative heights of the two waves.

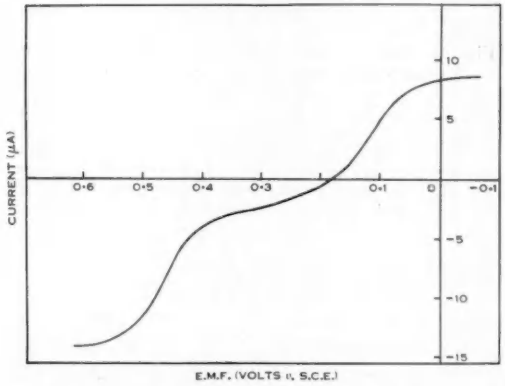



Fig. 6.—Wurster's blue. Wave from rotated platinum electrode. pH 4·7.

Variation of $E_{\frac{1}{2}}$ with pH was linear over the pH range 2·5–5·3 for both the small and large wave. For the small wave a value of 55 mV/pH unit and for the large wave 30 mV/pH unit were obtained. The shift of 30 mV/pH unit is low for a one-electron system.

(iii) *Rotated Platinum Microelectrode.*—Recourse was had to a rotated platinum microelectrode to ascertain whether the stationary electrode was responsible for the anomalous results.

As before, two waves were obtained but the anodic wave was the same height as the cathodic wave (Fig. 6). At pH's greater than 6·0 the anodic wave increased in height, until from pH 7·2 to 8·0 the ratio of the height of the anodic to the cathodic wave was 2 : 1. Half-wave potentials followed closely

those obtained with the dropping mercury electrode. A comparison of some slopes and half-wave potentials with those obtained with the latter electrode follows :

Cathodic Wave

| pH .. .. | 3·9 | 4·3 | 4·9 | 5·4 | 6·0 |
|---|---|---|---|---|---|
| $E_{\frac{1}{2}}$ (Pt) .. .. | 0·166 | 0·140 | 0·115 | 0·078 | 0·052 |
| $E_{\frac{1}{2}}$ (Hg) .. .. | 0·175 | 0·150 | 0·120 | 0·090 | 0·060 |
| Slope (Pt) (mV) .. | 66 | 68 | 66 | 72 | 65 |
| Slope (Hg) (mV) | 60 | 60 | 63 | 69 | 60 |

Reproducibility of polarograms was much better than that obtained with the stationary platinum electrode.

The slope of the plot of $E$ *v.* $\log i/(i_d - i)$ was linear at all pH values.

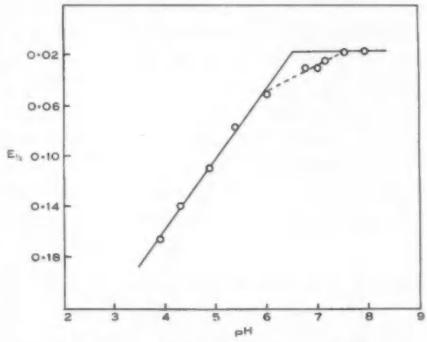



Fig. 7.—Wurster's blue. Half-wave potential *against* pH ; cathodic wave from rotated platinum electrode.

In the table below the $E_{\frac{1}{2}}$ and the slope of the plot of $E$ against $\log i/(i_d - i)$ for the anodic wave at pH 3·9, 4·6, and 5·3 is compared with the values given by the stationary platinum electrode.

| pH .. .. .. .. | 3·9 | 4·6 | 5·3 |
|---|---|---|---|
| $E_{\frac{1}{2}}$ (stat. Pt) .. .. | 0·44 | 0·42 | 0·39 |
| $E_{\frac{1}{2}}$ (rot. Pt) .. .. | 0·465 | 0·453 | 0·441 |
| Slope (stat. Pt) (mV) .. | 60 | 60 | 60 |
| Slope (rot. Pt) (mV) .. | 59 | 64 | 55 |

As limiting currents were very much larger than those obtained with the dropping mercury electrode and with the stationary platinum electrode, the potential drop due to the resistance of the electrolyte was considerable. Both the half-wave potentials and the slopes of the log plots have been corrected for this effect (" $iR$ drop ").

The $E_{\frac{1}{2}}$ of cathodic wave given by the radical varied with pH (Fig. 7). $E_{\frac{1}{2}}$/pH relationship followed closely that observed with the dropping mercury electrode.

From pH 3·9–6·0 the slope was 55 mV/pH unit. Between pH 6·0 and 7·5 the average slope was 23 mV/pH unit. Above 7·5 there was no significant change of $E_{\frac{1}{2}}$. As before, the range pH 6·0–7·5 must be regarded as a transition range.

Again the $E_{\frac{1}{2}}$/pH relationship for the anodic wave gave a value too low for a one-electron system (Fig. 8). The cathodic and anodic waves were approximately of equal height from pH 3·9–6·0 and the $E_{\frac{1}{2}}$/pH slope dependence was linear with a slope of 18 mV/pH unit. From pH 6·8 to 8·0 no change in $E_{\frac{1}{2}}$ occurred, however, the anodic wave increased in height. A break occurs in the $E_{\frac{1}{2}}$/pH graph at pH 6·7. If this break could be interpreted as due to a dissociation of the reduced form, it would agree quite well with the value obtained potentiometrically by Michaelis and Hill (1933) of pH 6·5.

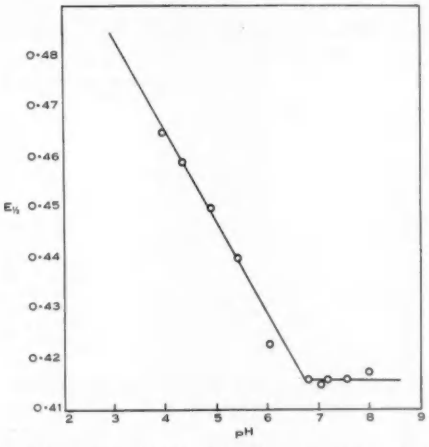



Fig. 8.—Wurster's blue. Half-wave potential *against* pH; anodic wave from platinum electrode.

There does not appear to be any obvious explanation for this increase in wave height and the low $E_{\frac{1}{2}}$/pH dependence of the wave.

(iv) *Amperometric Titration.*—Amperometric titration of the amine dihydrochloride with bromine water showed that the addition of *two* equivalents of bromine produced the maximum (steady) cathodic current, which was in fact the same as that obtained from the same molar concentration of the Wurster salt at the same potential. Addition of bromine water to the Wurster salt, as expected, did not increase the cathodic current. As theoretically only *one* equivalent of bromine is necessary to produce the radical, the above observation must have its explanation in the extreme lability of the di-imine with which the intermediate radical is in equilibrium.

The radical from *NNN'N'*-tetramethyl-*p*-phenylenediamine is known to be quite stable in acid solution (Michaelis, Schubert, and Granick 1939). Hence

one would expect to obtain a polarogram having equal anodic and cathodic parts. With the mercury electrode a single cathodic wave involving one electron is observed. Both the stationary and rotated platinum electrodes reveal an expected anodic wave. However, only the rotated platinum electrode produces an anodic wave equal in height to the cathodic wave. Logarithmic analysis of the anodic wave obtained with the rotated platinum electrode indicates a one-electron step, but the $E_{\frac{1}{4}}$/pH dependence is too low for a one-electron system (18 mV/pH unit). For a one-electron system the $E_{\frac{1}{4}}$/pH dependence can only be 0, 60 mV/pH unit, or some multiple of the latter figure.

Since the other evidence indicates that the anodic wave is a one-electron step, it seems some other explanation must be found for the low $E_{\frac{1}{4}}$/pH dependence.

The almost purely cathodic wave produced by the radical at the dropping mercury electrode develops a larger anodic portion on standing; the overall height is constant. Also the initial purely anodic wave given by the amine changes to a wave possessing the same relative ratio of anodic to cathodic part as the wave from the radical. Atmospheric oxidation of the base produces the latter change. Both the polarographic wave and the absorption spectrum suggest the radical is being reduced to the amine. An equilibrium is apparently set up between the oxidation of the base and the reduction of the radical. The mechanism of the reduction is not clear, but it may proceed via the di-imine with which the radical is in equilibrium. Michaelis, Schubert, and Granick (1939) found that the extremely unstable di-imine reverted to the radical in acetic acid solution (the initially colourless di-imine returned to the deep blue of the radical), but no explanation was given.

### (*d*) *Wurster Salt of 2,3,5,6-Tetramethyl*-p-*phenylenediamine*

The Wurster salt was very stable in the solid state.

(i) *Dropping Mercury Electrode.*—At concentrations higher than $2\times10^{-3}$M the solution turned from yellow to green indicating polymerization (Michaelis and Granick 1943) and on standing for a short time yellow needle-like crystals of duroquinone were formed (LuValle, Glass, and Weissberger 1948). At lower concentrations the solution was yellow and no precipitation occurred.

A fresh solution of the Wurster salt produced an anodic and a cathodic wave. On aging, the cathodic wave increased and the anodic wave decreased in height until only the cathodic wave remained (Fig. 9). The total wave height remained the same throughout.

The polarogram obtained from a fresh solution of the amine consisted of an anodic wave of the same $E_{\frac{1}{4}}$ and slope as that from the radical. Aging produced first an anodic and a cathodic wave entirely analogous to those produced by the radical and finally a solely cathodic wave (Fig. 10).

Both waves were diffusion controlled because

(i) Limiting current was proportional to the (height of mercury)$^{\frac{1}{2}}$.

(ii) Limiting current was proportional to concentration over the range 0·5–0·125 mM.

A stationary platinum electrode did not reveal any further waves.

A graph of log $(i/i_d-i)$ *v.* $E$ was linear at all pH's studied for both the anodic and cathodic waves. For the cathodic wave the slope was close to 37 mV/log unit from pH 3·9–6·4 and 31 mV/log unit for pH 7·1–9·35.

The anodic wave had a slope close to 45 mV from pH 3·9–5·9 which then slowly decreased from 40 mV at pH 6·4 to a steady value of 32 mV at pH 7·96.

A value of 30 mV/log unit applies to a two-electron reversible wave at 25 °C. In the case of both waves this value is approached at high pH's. The relatively high value of 45 mV for the anodic wave in the range pH 3·9–5·9 is most likely due to intermediate radical formation.

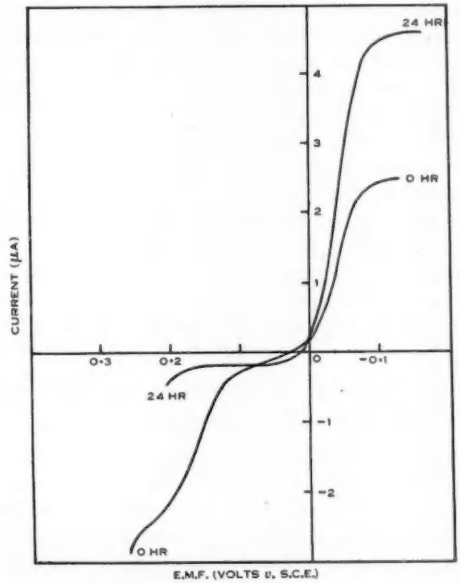



Fig. 9.—Wurster salt from diaminodurene. Change of wave with time; pH 4·6.

Application of the Ilkovič equation also indicated a two-electron step. As before, the main difficulty was the calculation of the diffusion coefficient of the Wurster cation. The diffusion coefficient was evaluated by conductance measurements on solutions of the Wurster salt and on the amine dihydrochloride in the presence of excess amine. Values for $D^0$ were $11\cdot2\times10^{-6}$ and $8\cdot3\times10^{-6}$ $cm^2\,sec^{-1}$ respectively. Since conductances increased rapidly in the case of the radical and were quite steady in the case of the amine dihydrochloride, the latter figure was accepted as correct.

Now,

$$i_d=2\cdot60\ \mu A \quad m^{2/3}t^{1/6}=1\cdot619\ mg^{2/3}\,sec^{-1/2},$$
$$c=0\cdot5\ mM \quad D=8\cdot3\times10^{-6}\ cm^2\,sec^{-1},$$

therefore,

$$n = 1 \cdot 84 \text{ electrons}$$

that is, two electrons were involved in each step.

Variation of $E_{\frac{1}{2}}$ with pH for both waves suggested that two electrons and two protons were involved in the electrode reaction over the pH range 3·9–9·35. A graph of $E_{\frac{1}{2}}$ as a function of pH had a slope of 53 mV/pH unit for the anodic wave and 59 mV/pH unit for the cathodic wave (Figs. 11, 12).

It appears that even in solutions of high pH two protons are still involved in the electrode reaction.

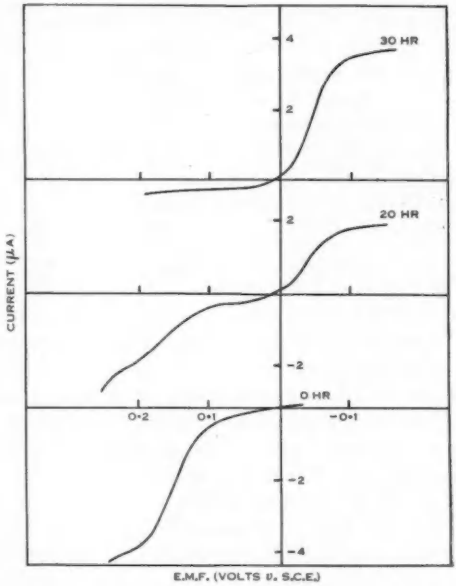



Fig. 10.—Diaminodurene. Change of wave with time; pH 4·6.

The anodic wave was due to the amine. Duroquinone was probably responsible for the cathodic wave as the $E_{\frac{1}{2}}$ at pH 6·24 (−0·137 V) was the same as that found for duroquinone (Page 1943), −0·140 V in a solution of apparent pH 6·24. Yellow needles which separated from the solution on standing were shown to be duroquinone by the absorption spectrum.

(ii) *Amperometric Titrations.*—Amperometric titration of the amine with bromine water showed that two equivalents of bromine were required for the amine and one equivalent for the Wurster salt to give the maximum cathodic current. Oxidation of the radical produced a current equal to that obtained by the complete oxidation of the same molar concentration of the amine.

This behaviour is in agreement with expectations as the duroquinone formed from the hydrolysis of the di-imine is perfectly stable.

From the polarographic behaviour of the radical it is clear that it does not exist as such in aqueous solution. The green colour formed at higher concentrations appears to indicate that the polymer is more stable than the radical. At all concentrations, however, only waves produced by the diamine and duroquinone are observed. Duroquinone is formed by the hydrolysis of the unstable di-imine.

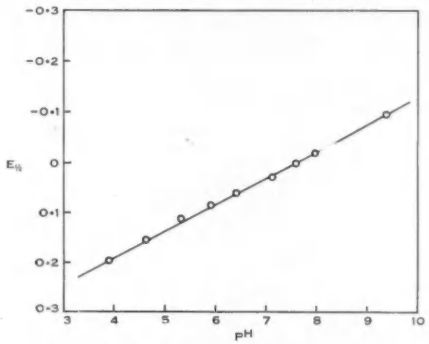



Fig. 11.—Wurster salt from diaminodurene. Half-wave potential *against* pH; anodic wave.

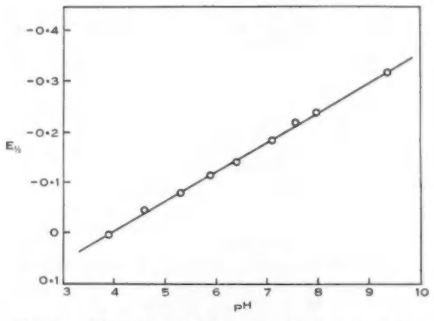



Fig. 12.—Wurster salt from diaminodurene. Half-wave potential *against* pH; cathodic wave.

## IV. Discussion

One of the most striking features which emerge from the present studies is the dramatic effect of a change of solvent upon the stability of Wurster salts. Some salts which Michaelis and his collaborators found to be quite stable in methanol-acetic acid-water become much less so in acetate buffers. Wurster's blue remains fairly stable, but its stability is much less than it is in distilled water, and is affected by the pH of the solution. It is noteworthy also that Wurster's blue is quite labile in some organic solvents. Solutions in hexanol are pink, and in pyridine and quinoline there is quite a rapid colour change (to be

expected because of the basic character of these solvents). The semiquinone formation constant for Wurster's blue, as deduced qualitatively from the separation of the waves, is approximately 20,000 at pH 4·5, much larger than the value (approximately 4) deduced by Michaelis from his titration curves.

The instability of the Wurster salt from *p*-phenylenediamine is confirmed, but from the polarogram, Michaelis' conclusion that this reflects the instability of the fully oxidized quinonoid structure is supported. Wurster's red also appears less stable in the buffer solutions studied than in the organic solvent.

The Wurster salt from *p*-diaminodurene presents an interesting situation. In Michaelis' work, in methanol-acetic acid, the Wurster salt and the di-imine compound were both sufficiently stable to produce oxidation steps in the titration with bromine. In the present work, it was not possible to detect the Wurster salt in solution, either by the polarogram, or by the absorption spectrum. The polarogram was that to be expected from a mixture of diamine and duroquinone, and the absorption spectrum showed no sign of the strong bands at about 450–480 mμ characteristic of the free radical. Duroquinone and *p*-diaminodurene are both devoid of pronounced absorption in this region. The bands of duroquinone are at 432 mμ ($\varepsilon=24\cdot6$) and 327 mμ ($\varepsilon=470$) in hexane; in water the positions of the maxima are shifted slightly.

Where polarographic waves were obtained which could be compared, reduction potentials agreed quite well with Michaelis' values at the smooth platinum electrode. This indicates that the species being reduced exhibit comparatively small over-voltages at the mercury electrode. The agreement between the values of half-wave potentials obtained at the dropping mercury electrode and the platinum microelectrode supports this conclusion. It appears that it would be worth while to persevere with attempts to study the polarographic behaviour of Wurster salts in non-aqueous solvents, and some work is projected in this field. It is also intended to study the electrical conductance of solutions of the salts in non-aqueous solvents in order that a more exact value of the diffusion coefficient may be obtained in the absence of possible hydrolysis.

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# SOME STUDIES IN INORGANIC COMPLEXES

## I. THALLIUM(III)

By G. J. SUTTON*

[*Manuscript received September 27, 1957*]

*Summary*

Investigations have been made into the structures of some thallium(III) complexes of 2,2′-dipyridyl, 1,10-phenanthroline, and ethylenediamine. From the substances investigated, the results indicate that where there are one or two molecules of ligand to one of thallic halide the complexes are uni-univalent electrolytes of the type $[TlX_2B_2][TlX_4]$ or $[TlX_2B_2]X$ respectively, in which B is chelating base and X is halide ion.

## I. INTRODUCTION

The thallic complexes of ethylenediamine described by Hieber and Sonnekalb (1928) included the chloro derivatives $TlCl_3.en_3.3H_2O$, $TlCl_3.en_2.H_2O$, $TlCl_3.en.H_2O$; two bromo complexes $TlBr_3.en_3.3H_2O$ and $TlBr_3.en$; and the iodo complex $TlI_3.en$. The only physical measurement recorded was that of a molecular weight determination of the latter bronze coloured compound in nitrobenzene, for which the observed result (589·5) at a low concentration (1 per cent.) was in good agreement with that of the theoretical value for the complex as a non-ionic monomer (644·7). However, from this result these workers concluded that the degree of dissociation was 0·093 and that the ethylenediamine was only partly attached, although the depression of freezing point was small. Hence, it was decided to carry out further investigations with these compounds as well as those with dipyridyl and phenanthroline, the preparation of which has been described previously by Sutton (1951). Using nitrobenzene as a solvent, electrical conductivity and ionic weight determinations by the cryoscopic method were carried out with the dipyridyl and phenanthroline complexes and with the ethylenediamine complexes $TlBr_3.en$ and $TlI_3.en$. It was found that the other thallic complexes of ethylenediamine were too insoluble in nitrobenzene, bromobenzene, or in ethylene dibromide for accurate determinations to be made. Ionic weight determinations by the ebullioscopic method using acetone as a solvent were unsatisfactory due to decomposition, since in this solvent hydroxyl groups may be formed by hydrogen bonding. The conductivity and ionic weight determinations in nitrobenzene of the thallic complexes of the type $TlX_3.B$ showed that the substances are dimeric electrolytes $[TlX_2B_2]^+[TlX_4]^-$, whilst those of the type $TlX_3.2B$ are the electrolytes $[TlX_2B_2]^+[X]^-$. The former structure is also in agreement with the molecular weight for the complex $TlI_3.en$ as a monomer, which would be the same as the

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ionic weight of the substance as a dimeric electrolyte. It is interesting to note that whilst complexes of the type $[TlX_2B_2]^+[X]^-$ were obtained with ethylenediamine as ligand the only compounds of this type with dipyridyl or phenanthroline isolated were the iodides. Precipitation of the cation complexes with the large $[TlX_4]^-$ ions takes place very readily and the presence of the latter anions was confirmed by precipitation with triphenylmethylarsonium cation. Furthermore, by avoiding excess iodide ion and base and working in more concentrated ethanolic solutions, the iodo complexes of dipyridyl and phenanthroline $[TlI_2B_2]^+[TlI_4]^-$ were isolated. The conductivity and ionic weight determinations are summarized in Table 1, all measurements having been made in nitrobenzene, excepting that marked with an asterisk.

Since the mechanism of coordination depends on the structures of the thallic halides themselves, reference to the structures of these compounds is included. These structures together with that of dimethyl thallium(III) iodide were investigated by Berry *et al.* (1928). Conductivity determinations in water, methanol, and in acetonitrile were carried out in conjunction with studies of absorption spectra. However, the results gave marked deviations from Onsager's rule using water or methanol as solvents and are non-diagnostic of structure at low concentrations, whilst with acetonitrile as solvent coordination was very likely. At higher concentrations in these solvents the results were in approximate agreement with half what would be expected for uni-univalent electrolytes on the assumption that the thallic halides are monomers. From these results the existence of dimeric structures $[TlX_2]^+[TlX_4]^-$ in solutions is indicated and this has been confirmed by conductivity measurements in nitrobenzene at concentrations from 0·002 to 0·05M. At extremely low concentrations apparent dissociation of the complex ions occurs, but this could be partly due to working outside the limits of accuracy of the instrument used. The dissociation constants of the ions $[TlCl_4]^-$ and $[TlBr_4]^-$ were determined potentiometrically by Benoit (1949) in a study of complex chlorides and bromides of thallium(III), and thallium-halogen bonding is also indicated from a study of the unit cell dimensions of thallic chloride (Templeton and Carter 1954). It has also been reported by Syrkin and Dyatkina (1950) that the conductivity of fused chloride is zero, which suggests that in the solid state the compound has a very high degree of homopolar character. On solution in solvents such as water, methanol, or ethanol, it is likely that the thallic halides form octahedral complexes $[TlX_2Sol_4]^+[TlX_4Sol_2]^-$, in which Sol represents coordinating solvent molecules. Replacement of the solvent molecules in the cation complexes may then be effected by the more powerful chelating ligands, the mechanism of these reactions being uncertain. Due to lability, transformation from complexes containing one molecule of ligand per molecule of thallic salt (as monomer) to those containing two molecules of ligand and vice versa may then take place as a result of the following equilibrium (solvent molecules being omitted):

$$[TlX_4]^- + 2B \rightleftarrows [TlX_2B_2]^+ + 2[X]^-.$$

Since the complexes $[TlI_2B_2]^+[TlI_4]^-$ give no reaction with starch in solution with aqueous potassium iodide and ethanol, it appears that the formation of

TABLE 1

MOLECULAR CONDUCTIVITIES AND IONIC WEIGHTS

| Substance | M Conductivities | | Ionic Weights | | |
|---|---|---|---|---|---|
| | (mhos) | M Conc. | Found | % Conc. | Calc. |
| $(Tlen_2Br_2)(TlBr_4)$ .. | 22·1 | 0·0052 | | | |
| $(Tlen_2I_2)(TlI_4)$ .. .. | 19·4 | 0·0080 | 512 | 0·20* | 645 |
| | 20·0 | 0·0050 | | | |
| $(Tlphen_2I_2)I$ .. .. | 18·1 | 0·0133 | 451 | 0·27 | 473 |
| | 18·2 | 0·0092 | 486 | 0·87 | 473 |
| | 18·9 | 0·0011 | 524 | 1·26 | 473 |
| $(Tldipy_2I_2)I$ .. .. | 19·2 | 0·0037 | 418 | 0·47 | 449 |
| | 19·3 | 0·0036 | | | |
| $(Tlphen_2Cl_2)(TlCl_4)$ .. | 18·6 | 0·0029 | 451 | 0·22 | 490 |
| | 19·6 | 0·0019 | 425 | 0·17 | 490 |
| $(Tlphen_2Br_2)(TlBr_4)$ .. | 18·1 | 0·0156 | 510 | 0·15 | 624 |
| | 19·2 | 0·0053 | 555 | 0·097 | 624 |
| | 19·8 | 0·0013 | | | |
| | 20·8 | 0·0006 | | | |
| $(Tlphen_2I_2)(TlI_4)$ .. | 18·3 | 0·0102 | 703 | 0·26 | 765 |
| | 18·8 | 0·0034 | | | |
| $(Tldipy_2Cl_2)(TlCl_4)$ .. | 18·7 | 0·0031 | 455 | 0·20 | 467 |
| | 18·8 | 0·0036 | 425 | 0·17 | 467 |
| | 19·6 | 0·0011 | | | |
| | 19·8 | 0·0010 | | | |
| $(Tldipy_2Br_2)(TlBr_4)$ .. | 19·2 | 0·0045 | 552 | 0·28 | 600 |
| $(Tldipy_2I_2)(TlI_4)$ .. | 17·2 | 0·0044 | 683 | 0·30 | 741 |
| | 17·7 | 0·0011 | | | |
| $[Ph_2MeAs][TlCl_4]$ .. | 25·1 | 0·0074 | 342 | 0·49 | 334 |
| $[Ph_2MeAs][TlBr_4]$ .. | 26·4 | 0·0060 | 372 | 0·25 | 422 |
| $[Ph_2MeAs][TlI_4]$ .. | 24·8 | 0·0051 | 475 | 0·19 | 516 |

* This measurement was not made in nitrobenzene.

periodide ion in " thallic iodide " is due to decomposition of the di-iodo thallic cation as follows (omitting attached solvent molecules):

$$[TlI_2] \rightleftarrows Tl^+ + I_2.$$

With the less negative arsenic as donor atom using the ligands dimethyl phenylarsine or the more powerful *o*-phenylenebisdimethylarsine, no complexes of thallium(III) were obtained, but reduction to thallous salts took place.

Further studies on complex formation with non-transition elements using the ligands *o*-phenylenebisdimethylarsine, 2,2′-dipyridyl and 1,10-phenanthroline are being carried out and it is hoped to publish the results of these investigations, with special reference to group 5B, subsequently.

## II. Experimental

The molecular conductivity measurements were determined in pure nitrobenzene at 25 °C using a conductivity-measuring bridge Philoscope model GM4249/01 and cell GM4221. The nitrobenzene was purified by filtering frozen nitrobenzene, discarding the filtrate, treating with calcium chloride, and redistilling. Successive products so treated had specific conductances varying from $0{\cdot}14\times10^{-6}$ to less than $10^{-7}$ mhos, and corrections for these low conductances were made. The acetone was purified by precipitation as bisulphite compound, decomposing the latter after filtering using sodium carbonate solution, drying over calcium sulphate, and redistilling. In most cases the solubilities of the thallium(III) ethylenediamine complexes were found to be too low for the determination of ionic weights in nitrobenzene.

(*a*) *Dibromobisethylenediamine Thallium(III) Tetrabromothallate(III).*—Thallic bromide tetrahydrate (15 mmoles) in water (30 ml) was treated with ethylenediamine (15 mmoles). The solution was allowed to stand in a vacuum desiccator until colourless acicular crystals of the complex were precipitated. The solution was decanted and the crystals were dried in a vacuum desiccator over calcium chloride (yield 4·16 g) (Found: C, 4·67; H, 1·26; Br, 47·5; Tl, 40·8%. Calc. for $C_2H_8N_2Br_2Tl$: C, 4·76; H, 1·59; Br, 47·5; Tl, 40·5%).

(*b*) *Di-iodobisethylenediamine Thallium(III) Tetraiodothallate(III).*—The complex was obtained by the addition of excess potassium iodide to an aqueous solution of the aforementioned bromo complex. Purification was effected by washing the bronze-yellow powder which precipitated with successive small portions of water, the yields being almost quantitative (Found: C, 3·92; H, 1·47; I, 59·6; Tl, 31·6%. Calc. for $C_2H_8N_2I_2Tl$: C, 3·72; H, 1·25; I, 59·9; Tl, 31·7%).

(*c*) *Dichlorobisphenanthroline Thallium(III) Tetrachlorothallate(III).*—Thallic chloride tetrahydrate (1 mmole) in water (10 ml) was treated with phenanthroline hydrate (1 mmole) in ethanol (2 ml) and the white precipitate which formed was separated by centrifuging and drying over sulphuric acid in a vacuum desiccator (Found: Cl, 21·4; Tl, 41·7%. Calc. for $C_{12}H_8N_2Cl_2Tl$: Cl, 21·7; Tl, 41·6%).

(*d*) *Dibromobisphenanthroline Thallium(III) Tetrabromothallate(III).*—Beginning with thallic bromide tetrahydrate instead of the chloride, the latter procedure was repeated (Found: C, 22·9; H, 1·4; Br, 38·2%. Calc. for $C_{12}H_8N_2Br_2Tl$: C, 23·1; H, 1·7; Br, 38·5%).

(*e*) *Di-iodobisphenanthroline Thallium(III) Tetraiodothallate(III).*—Thallic chloride tetrahydrate (0·382 g; 1 mmole) in water (10 ml) was treated with a mixture of phenanthroline monohydrate (0·198 g; 1 mmole) and sodium iodide (0·450 g; 3 mmoles) in 90% aqueous ethanol (10 ml) and water (10 ml) added with stirring. The orange precipitate formed, settled rapidly, and was separated by centrifuging and re-precipitating from ethanol by the addition of water. The orange-red prisms, which resulted after drying over sulphuric acid in a vacuum desiccator, were soluble in methanol, ethanol, and acetone (yield 0·754 g) (Found: C, 18·7; H, 1·4; I, 49·3%. Calc. for $C_{12}H_8N_2I_2Tl$: C, 18·9; H, 1·1; I, 49·7%).

(*f*) *Di-iodobisphenanthroline Thallium(III) Iodide.*—The latter procedure was repeated, but phenanthroline monohydrate (0·396 g; 2 mmoles) was added and excess sodium iodide (1 g) was used (Found: C, 30·2; H, 2·1; I, 40·0%. Calc. for $C_{24}H_{16}N_4I_2Tl$: C, 30·5; H, 1·8; I, 40·3%).

(*g*) *Dichlorobisdipyridyl Thallium(III) Tetrachlorothallate(III).*—The salt was prepared by the same procedure as that for the corresponding phenanthroline complex using dipyridyl (1 mmole) in lieu of phenanthroline (Found: C, 25·8; H, 1·8; Cl, 22·7%. Calc. for $C_{10}H_8N_2Cl_2Tl$: C, 25·7; H, 1·7; Cl, 22·9%).

(*h*) *Dibromobisdipyridyl Thallium(III) Tetrabromothallate(III).*—Using the aforementioned experimental procedure the complex was prepared by allowing thallic bromide tetrahydrate

(1 mmole) and dipyridyl (1 mmole) to react (Found: Br, 40·2; Tl, 34·4%. Calc. for $C_{10}H_8N_2Br_3Tl$: Br, 40·0; Tl, 34·1%).

(*i*) *Di-iodobisdipyridyl Thallium(III) Tetraiodothallate(III).*—Thallic chloride tetrahydrate (0·382 g; 1 mmole) in water (10 ml) was treated with dipyridyl (0·156 g; 1 mmole) in ethanol (5 ml) and sodium iodide (0·450 g; 1 mmole) in water (5 ml) added with stirring. The orange-red precipitate which formed was separated by centrifugation, and after washing twice with cold water and then with 50% alcoholic ether it was dried at 100 °C and then in a vacuum desiccator over sulphuric acid. The orange-red prisms which resulted (0·660 g) were found to be soluble in methanol, ethanol, and acetone (Found: I, 51·8; Tl, 27·4%. Calc. for $C_{10}H_8N_2I_3Tl$: I, 51·4; Tl, 27·5%).

(*j*) *Di-iodobisdipyridyl Thallium(III) Iodide.*—The complex was prepared similarly to the corresponding phenanthroline salt by allowing thallic chloride tetrahydrate (1 mmole) to react with dipyridyl (2 mmoles) in the presence of excess iodide ion (Found: I, 19·9; Tl, 31·7%. Calc. for $C_{20}H_{16}N_4I_3Tl$: I, 19·7; Tl, 31·8%).

(*k*) *Triphenylmethylarsonium Tetrachlorothallate(III).*—The salt was obtained by dissolving the complex dichlorobisphenanthroline thallium(III) tetrachlorothallate(III) in the smallest quantity of ethanol, filtering, and adding an excess of a concentrated solution of triphenylmethylarsonium chloride in ethanol. On evaporating to half volume and adding water the salt was precipitated as a colourless microcrystalline powder. It was separated, washed with water and then with ethanol, and dried in a vacuum desiccator over concentrated sulphuric acid (Found: C, 34·1; H, 2·9; Cl, 21·5%. Calc. for $C_{19}H_{18}AsCl_4Tl$: C, 34·2; H, 2·7; Cl, 21·3%). A similar product was obtained from the corresponding dipyridyl complex. The salt was found to be stable to above 300 °C.

(*l*) *Triphenylmethylarsonium Tetrabromothallate(III).*—The above experimental procedure was repeated using dibromobisdipyridyl thallium(III) tetrabromothallate(III) instead of the chlorophenanthroline complex. The corresponding bromophenanthroline complex gave a similar product (Found: C, 26·9; H, 2·3; Br, 37·8%. Calc. for $C_{19}H_{18}AsBr_4Tl$: C, 26·9; H, 2·2; Br, 37·9%).

(*m*) *Triphenylmethylarsonium Tetraiodothallate(III).*—The aforementioned experimental procedure was repeated with di-iodobisphenanthroline thallium(III) tetraiodothallate(III) and with the corresponding dipyridyl complex. The orange product which resulted proved that the $[TlI_4]'$ ion is orange and that the colour of the iodo complexes is due at least in part to this ion (Found: C, 22·1; H, 1·8; I, 48·5%, 49·0%. Calc. for $C_{19}H_{18}AsI_4Tl$: C, 22·1; H, 1·8; I, 49·1%).

## III. Acknowledgment

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# THE ADSORPTION OF ASPARTIC ACID AND GLYCINE ON SPARINGLY SOLUBLE INORGANIC SOLIDS

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*Summary*

An investigation has been made of the adsorption of aspartic acid and glycine on a series of natural and synthetic sparingly soluble inorganic solids. The amino acids have been analysed by a photographic development of the Fisher-Parsons-Morrison relationship found to exist for paper chromatograms.

Aspartic acid was found to be adsorbed in greater amounts than glycine. Natural samples showed higher adsorptive capacities for both acids than did the synthetic samples. Adsorption capacities of the solids investigated were considerably higher than those found by previous workers for similar solids. No correlation has been found between adsorptive capacities and known electrokinetic properties of the adsorbents.

## I. Introduction

Because of their alleged poor selectivity and low adsorptive capacity (Bottger 1939), sparingly soluble inorganic solids have not been extensively studied for their chromatographic suitability for amino acid adsorption. Hamoir (1943, 1945) and Tarte (1945) investigated the adsorption and elution properties of precipitated silver sulphide and barium sulphate respectively, but found their compounds possessed a low adsorbing power (1/10,000). However, they showed that suitable activation of the adsorbents with lattice cations produced precipitates that would selectively adsorb certain acids. These authors used a large number of acids on a single adsorbent, but the present research was performed in the reverse manner, namely, investigation of the adsorptive behaviour of two simple acids (aspartic acid and glycine) on a large number of solids. It was considered that such information could possibly be related to the surface physical properties of the adsorbent, but no definite relationship has been found to exist.

All adsorptions were performed on unactivated samples, whilst the amino acid contents of the various solutions were estimated quantitatively by means of paper chromatography using the spot-area relationship reported by Fisher, Parsons, and Morrison (1948).

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## II. Experimental

### (*a*) *Adsorbents*

The 17 solids, given in Table 1, were used as adsorbents.

Table 1

AMINO ACID ADSORBENTS

| Adsorbent | Type |
|---|---|
| ZnS (sphalerite) .. .. .. | Natural and synthetic |
| PbS (galena) .. .. .. | Natural and synthetic |
| $PbMoO_4$ (wulfenite) .. .. | Natural and synthetic |
| $PbSO_4$ (anglesite) .. .. | Natural and synthetic |
| $BaSO_4$ (barite) .. .. .. | Natural and synthetic |
| $PbCrO_4$ (crocoite) .. .. | Natural, synthetic, and fused |
| $BaCrO_4$ .. .. .. .. | Synthetic |
| Alumina .. .. .. .. | Activated |
| Zeolite .. .. .. .. | Synthetic |
| Exchange resin .. .. .. | "Amberlite IRA 400" |

These samples can be divided into three groups: (i) natural samples, (ii) artificial samples, (iii) sundry adsorbents.

(i) *Natural Samples.*—The samples used were crystalline; the ZnS and PbS were from Broken Hill, and the lead chromate from Mt. Dundas, Tasmania.

(ii) *Artificial Samples.*—The ZnS, fused $PbCrO_4$, and $BaCrO_4$ samples were B.D.H. products. The remainder were prepared in a state of high purity, lead sulphide by fusion of lead and sulphur and lead molybdate, lead sulphate, barium sulphate, and lead chromate by standard gravimetric procedures. All reagents used were of A.R. quality and the solutions were prepared in twice-distilled water. The solids were ground to a B.S.S. mesh size +100–150.

(iii) *Sundry Adsorbents.*—The activated alumina was a commercial granular product (Sulphates Ltd.) and had been activated by heating at 900 °C for 3 hr. The synthetic zeolite was a Hopkins and Williams product and was marketed in coarse granules under the name of "Permutit". The strongly basic anion resin was supplied by Rohm and Haas Ltd., and was used in the hydroxyl form.

### (*b*) *Amino Acid Estimation*

The technique employed for the amino acid analysis followed that originally proposed by Consden, Gordon, and Martin (1944), except an ascending method of solvent migration was used (Williams and Kirby 1948).

(i) *Solvents.*—The solvent used was phenol purified by the method of Hillis (1950) to yield a completely colourless product. Over the course of the several months during which this work was performed, the phenol crystals were kept in closed porcelain jars and remained substantially colourless for the entire period. The mobile phase used consisted of 80 per cent. aqueous phenol which has been stated to give $R_F$ values that are less dependent on temperature than

is the case with the more common water-saturated phenol (Berry and Cain 1949).

(ii) *Identification.*—The spray used was 0·1 per cent. ninhydrin in water-saturated *n*-butanol containing 1 per cent. (v/v) pyridine (Phillips 1949).

(iii) *Preparation of Chromatograms.*—The solution to be analysed was applied to a Whatman No. 1 filter paper sheet as a 0·005 or 0·010 ml drop (depending on concentration) approximately 5 cm from the lower edge of the paper, and at least 4 cm from the adjacent spot. In many cases, the amino acid content of a 0·005 ml spot was below the minimum 3·0 μg above which quantitative linearity with spot area was found to exist. Therefore, it became necessary to achieve the desired concentration by successive application of 0·005 ml spots to the same position on the chromatogram. Such a procedure is only satisfactory when all spots are produced by the same volume and when each spot is dried before the next is applied. These spots were thoroughly dried under an infra-red lamp.

The paper sheet was used in cylindrical form with three thin wire links holding the edges apart. For the phenol to ascend 40–50 cm about 48 hr migrations were usually required. For most of the quantitative studies 20 cm was a sufficient and convenient distance for the movement of the solvent front, and this could be achieved during 1 day or overnight. On these chromatograms the spots were small, circular (especially glycine), and well separated, lending themselves admirably to area measurement. On removal from the tank the chromatograms were dried and developed using standard techniques (Berry and Cain 1949).

(iv) *Quantitative Measurements.*—Several general quantitative methods for amino acid estimation on paper chromatograms have been proposed using, for example, radioisotopes (Keston, Udenfriend, and Levy 1950), direct photometry (Rockland and Dunn 1949), copper phosphate (Woiwod 1949), colorimetric methods (Naftalin 1948), and spot area measurements (Fisher, Parsons, and Morrison 1948). In the Fisher, Parsons, and Morrison technique the logarithm of the acid content of the ninhydrin-developed spot has been found to bear a linear relationship to the area of such a spot. This relationship has been examined in the present investigation (O'Connor and Bryant 1951) and has been found to hold for the two amino acids studied. The method adopted has been to apply duplicate spots of three known concentrations of the standard acids (between 3 and 30 μg) to each chromatogram, and then triplicate spots from the unknown solution which must contain amounts of acid within this range.

The developed chromatogram was printed directly on Kodak reflex copying paper to produce a negative from which a black and white contact print was readily produced. On such a print the amino acid spots are more uniform in intensity and their edges are more clearly defined than on the original paper, and it was observed that the area of the spot on the photostat print was larger than that on the chromatogram. The spot area measurements were performed on the flattened print with a planimeter.

### (e) *Adsorption Experiments*

(i) *Column Adsorptions.*—Eight columns consisting of the samples listed in Table 2 were constructed.

In all cases the solids were ground to a B.S.S. mesh size of +52 −72 and then 10·00 g were packed wet into a 7 mm I.D. glass tube which had attached to one end a 1 mm bore glass stopcock. A small plug of glass wool was placed at the bottom of each column. Columns of artificial samples were not prepared because it was impossible to secure 10 g quantities of the crystals of the required mesh size. After packing, each column was washed with 200 ml of twice-distilled conductivity water, let stand in this water for 2 days, and then washed with a further 200 ml before use.

TABLE 2

COLUMN ADSORBENTS

| Adsorbent | Type | Adsorbent | Type |
|---|---|---|---|
| ZnS .. .. | Natural | $BaSO_4$ .. | Natural |
| PbS .. .. | Natural | $PbCrO_4$ .. | Natural |
| $PbMoO_4$ .. | Natural | $PbCrO_4$ .. | Fused |
| $PbSO_4$ .. .. | Natural | Zeolite .. | Synthetic |

Aspartic acid and glycine (100 mg of both) were dissolved in the same 2 l. of conductivity water and 200 ml aliquots were allowed to percolate slowly through each column. The influent pH of the mixed acid solution was 3·81. The rate of flow through the column was maintained at approximately 1 ml/min. After percolation of the amino acid solution a further 50 ml of water was passed through each column. The quantities of each amino acid in the influent and effluent were determined by evaporating each solution to approximately 3 ml and analysing chromatographically.

(ii) *Adsorption Rates.*—1 g samples (+200 mesh) of each of the solids listed in Table 1 were placed in 250 ml Erlenmeyer flasks and 100 ml of amino acid solution of the same composition as used in the column adsorptions added. The flasks were stoppered and shaken on an automatic shaker for 1 hr, this process being repeated several times daily. After an initial period of 5 days, 25 ml aliquots were removed at varying times from each flask and analysed chromatographically. Three such fractions were removed from each flask over a total period of 22 days.

## III. RESULTS

### (a) *Amino Acid Estimation*

Using the spot area-concentration relationship, it has been found that values for an unknown solution estimated on several chromatograms varied by not more than ±5 per cent. about the mean. In general the accuracy obtained within the range specified (3–30 μg) was somewhat better. As has been already reported (O'Connor and Bryant 1951), the accuracy obtained from replicates

on a single chromatogram has been found to be higher than when determinations are performed on several different sheets. On an individual chromatogram, the error has been found to be approximately ±1 per cent. The degree of accuracy obtained in the planimeter measurements is shown in Tables 3 and 4 for triplicate readings on duplicate spots of three applied concentrations for two different chromatograms.

TABLE 3

SPOT AREA MEASUREMENTS (PLANIMETER UNITS)

Chromatogram No. 6

| Amino Acid | Acid Concentration (μg/0·005 ml) | | | | | |
|---|---|---|---|---|---|---|
| | 3 | 3 | 5 | 5 | 7 | 7 |
| Aspartic Acid .. .. | 6 | 7 | 9 | 10 | 13 | 13 |
| | 7 | 8 | 9 | 12 | 15 | 12 |
| | 6 | 6 | 10 | 11 | 13 | 12 |
| Glycine .. .. .. | 17 | 18 | 20 | 21 | 23 | 24 |
| | 18 | 17 | 22 | 21 | 24 | 23 |
| | 16 | 17 | 22 | 20 | 24 | 24 |

TABLE 4

SPOT AREA MEASUREMENTS (PLANIMETER UNITS)

Chromatogram No. 9

| Amino Acid | Acid Concentration (μg/0·005 ml) | | | | | |
|---|---|---|---|---|---|---|
| | 5 | 5 | 19 | 19 | 20 | 20 |
| Aspartic Acid .. .. | 20 | 19 | 29 | 30 | 43 | 43 |
| | 21 | 21 | 31 | 31 | 43 | 43 |
| | 20 | 20 | 32 | 31 | 42 | 44 |
| Glycine .. .. | 34 | 34 | 47 | 45 | 56 | 56 |
| | 35 | 35 | 45 | 45 | 57 | 56 |
| | 34 | 34 | 44 | 45 | 55 | 57 |

It has been found that area measurements of the same concentration of one acid may vary appreciably between chromatograms, but for the same chromatogram the gradients obtained by plotting logarithm of acid concentration against the area of a spot for both acids are equal. In all cases aspartic acid exhibited smaller areas than glycine at the same concentration, whilst the spots of the latter acid were consistently more circular than the former.

### (*b*) *Column Adsorptions*

The capacity (mg/g adsorbent) of each of the solids used as columns are presented in Table 5.

TABLE 5

COLUMN ADSORPTIONS

| Adsorbent | Type | Amino Acid Adsorbed (mg/g adsorbent) | |
|---|---|---|---|
| | | Aspartic Acid | Glycine |
| ZnS .. | Natural | 0·41 | 0·24 |
| PbS .. .. | Natural | 0·32 | 0·33 |
| $PbMoO_4$ .. | Natural | 0·05 | 0·00 |
| $PbSO_4$ .. | Natural | 0·20 | 0·34 |
| $BaSO_4$ .. | Natural | 0·04 | 0·01 |
| $PbCrO_4$ .. | Natural | 0·00 | 0·00 |
| $PbCrO_4$ .. | Fused | 0·00 | 0·00 |
| Zeolite .. | Synthetic | 0·72 | 0·25 |

### (*c*) *Adsorption Rates*

The three 25 ml aliquots taken from each flask at varying times between 5 and 22 days were analysed by paper chromatography and the results are shown in Table 6. By comparison with the alumina, the zeolite, and the exchange resin, the inorganic solids have low acid adsorption values and much lower rates of adsorption. In all cases where comparative natural and artificial samples were used, the former showed higher adsorptive capacity for both aspartic acid and glycine (natural lead sulphate values not determinable). Natural zinc sulphide removed both acids in almost equal amounts which were much higher than similar values for any of the other samples.

Consideration of the total amino acid adsorption for the inorganic samples allows the following qualitative classification of relative adsorptive power to be made :

(i) High adsorption : Natural ZnS.

(ii) Medium adsorption : Natural $PbCrO_4$, artificial $BaCrO_4$, fused $PbCrO_4$, natural PbS, natural $PbMoO_4$, artificial $PbSO_4$.

(iii) Low adsorption : Artificial $PbMoO_4$, artificial $PbCrO_4$.

(iv) Incompletely determined adsorptions : Artificial PbS, artificial ZnS, natural $BaSO_4$, natural $PbSO_4$.

(v) No adsorption : Artificial $BaSO_4$.

As noted in Table 6 several anomalous effects prevented the complete analysis of all fractions. With reference to the *, the spot areas were excessively enlarged and much bigger than the spots of the original concentration (this was especially so with the natural lead sulphate). In the case of zinc sulphide (synthetic) the sprayed spots were considerably more red than normal, and their

TABLE 6

ADSORPTION RATES

| Adsorbent | Type | Progressive Total Amounts of Acid Adsorbed (mg) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Aliquot No. 1 | | | Aliquot No. 2 | | | Aliquot No. 3 | | |
| | | Aspartic Acid | Glycine | Time of Adsorption (hr) | Aspartic Acid | Glycine | Time of Adsorption (hr) | Aspartic Acid | Glycine | Time of Adsorption (hr) |
| ZnS .. .. | Natural | 1·96 | 1·80 | 120 | 2·20 | 2·16 | 336 | 2·20 | 2·18 | 469 |
| ZnS .. .. | Synthetic | * | 0·44 | 120 | * | 0·56 | 376 | * | 0·56 | 469 |
| PbS .. .. | Natural | 0·76 | 0·60 | 137 | 1·00 | 0·69 | 376 | 1·00 | 0·73 | 469 |
| PbS .. .. | Synthetic | † | 0·12 | 137 | † | 0·48 | 376 | Trace | 0·48 | 472 |
| $PbMoO_4$ .. .. | Natural | 0·84 | 0·64 | 137 | ‡ | ‡ | 376 | ‡ | ‡ | 469 |
| $PbMoO_4$ .. .. | Synthetic | 0·08 | 0·00 | 137 | 0·11 | 0·45 | 376 | 0·25 | 0·47 | 469 |
| $PbSO_4$ .. .. | Natural | * | * | 163 | * | * | 379 | * | * | 472 |
| $PbSO_4$ .. .. | Synthetic | 0·28 | 0·08 | 163 | 0·64 | 0·50 | 379 | 0·90 | 0·50 | 497 |
| $BaSO_4$ .. .. | Natural | † | 0·44 | 163 | ‡ | Trace | 379 | ‡ | ‡ | 497 |
| $BaSO_4$ .. .. | Synthetic | 0·00 | 0·00 | 163 | 0·00 | 0·00 | 379 | 0·00 | 0·00 | 497 |
| $PbCrO_4$ .. .. | Natural | 0·60 | 0·52 | 208 | 1·65 | 1·24 | 447 | 1·80 | 1·40 | 518 |
| $PbCrO_4$ .. .. | Synthetic | 0·40 | 0·00 | 186 | 0·67 | 0·00 | 450 | 0·67 | 0·00 | 518 |
| $PbCrO_4$ .. .. | Fused | 0·84 | 0·40 | 186 | 1·47 | 0·40 | 447 | 1·47 | 0·40 | 497 |
| $BaCrO_4$ .. .. | Synthetic | 1·20 | 0·51 | 186 | 1·41 | 0·51 | 447 | 1·67 | 0·73 | 518 |
| Alumina .. | Activated | 5·00 | 5·00 | 186 | | | | | | |
| Zeolite .. .. | Synthetic | 5·00 | 5·00 | 120 | | | | | | |
| Exchange resin .. | "Amberlite IRA 400" | 5·00 | 5·00 | 120 | | | | | | |

* Spots exhibited increased $R_F$ values and areas greater than corresponding to original concentrations.

† Exceedingly low amounts of acids.

‡ Complete absence of acids.

$R_F$ values (especially aspartic acid) had increased considerably. It appears significant that with both synthetic sulphides, aspartic acid determinations were impossible because of the effects mentioned above. In some cases, for example, † and ‡, complete or partial absence of acid spots has been attributed to mould, although in no case was its presence visible to the naked eye.

## IV. Discussion

At the pH of the amino acid solution used (pH=3·81), aspartic acid (pI=2·98) (Greenstein 1931) will exist principally as an anion and glycine (pI=6·06) (Owen 1934) principally as a cation. However, in all cases examined (except artificial lead chromate), there had been simultaneous adsorption of both anions and cations. Consideration of the total adsorbed amounts of amino acids (Table 6) and the solubility products of the various adsorbents shows that there is no correlation between these two quantities. This is more apparent when a comparison is made between the various samples of one adsorbent which should apparently have the same or similar solubility, but which show quite different adsorption capacities.

Hamoir (1943, 1945) used a column of flocculated $Ag_2S$ for the adsorption of various amino acids which could only be adsorbed when the flocculate had been activated in an excess of silver anion. Spherulites of barium sulphate, activated with 1 per cent. $BaCl_2$, have been found to adsorb glutamic and aspartic acids (Tarte 1945). Paneth (1928) has reported differences in the behaviour of natural and synthetic crystalline materials, for example, lead sulphide and barium sulphate. No exchange was observed between lattice cations in solution and on the surface of the crystals for the natural samples, but the artificially prepared samples exhibited marked exchange.

Two significant facts arise from a study of the capacities and selectivities of the amino acid adsorption by the sparingly soluble solids, namely,

(i) In all cases the natural samples showed greater adsorption capacities for both acids than did the corresponding synthetic samples, and

(ii) The quantities of aspartic acid adsorbed on each solid in both column and rate experiments were greater than the quantities of glycine adsorbed. (The only exception found was the case of lead sulphate in the column experiments.)

The greater adsorptive capacities of the natural samples can possibly be attributed to differences in composition or physical properties of the natural as distinct from the synthetic samples. That bulk composition is not the factor determining adsorptive capacity is shown by a study of the amounts of each acid adsorbed by both natural and synthetic samples of solids of the same composition. In addition, it would appear that impurities in bulk do not account for the variety of adsorptive capacities because quantitative spectrographic analyses showed that the natural and synthetic crystals were of comparable purities.

Undoubtedly the surface physical properties of the crystals are important in determining the amount of adsorption. Natural minerals often possess surfaces with compositions different from the composition of the bulk of the solid

(Rogers *et al.* 1948), for example, many sulphide minerals have surfaces which are partly oxidized. Galena and sphalerite both showed high adsorption capacities, the latter giving the highest capacity of all the solids studied.

It may be considered that adsorption is a function of the number of edges and corners on the surface of a crystal. However, it has been shown (Buchanan and Heymann 1948*a*, 1948*b*) that natural crystals of $BaSO_4$ have a greater surface regularity and smaller intrinsic $\zeta$-potential than crystals prepared from concentrated sulphuric acid, and thus the presence of edges and corners is in itself not alone sufficient to explain the difference in adsorbing capacities. Concurrently with these studies the electrokinetic properties of natural zinc sulphide, lead sulphate, barium sulphate, lead chromate, and synthetic lead sulphate, barium sulphate, and lead chromate and fused lead chromate were measured using the streaming potential method, but no correlation between $\zeta$-potential (surface charge density) and type and amount of amino acid adsorption was obtained.

Therefore, on the evidence available and in view of the paucity of published data on amino acid adsorption, it is difficult to unequivocally state the reason for the differences in adsorption behaviour of the solids, or for the greater adsorption of aspartic acid than glycine on all samples used in both column and rate experiments.

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# THE PROPERTIES AND STRUCTURES OF THE 1,8-TERPINS AND SOME RELATED COMPOUNDS

By C. S. Barnes*

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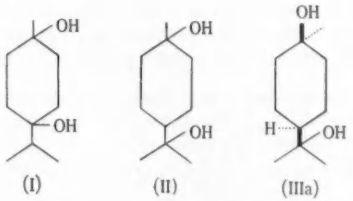
*Summary*

The mechanism of formation, and the chemical and hydrate forming properties of the 1,8-terpins are discussed. Configurations are assigned to the six 1,8-dihalogeno-*p*-menthanes, ethylnopinol, β-terpineol, *p*-menthan-1-ol, and homoterpin. It is suggested that the presently accepted configurations of the carveols and sobrerols may need to be reversed and that the structures of the *p*-menthane-2,8-diols need revision.

## I. Introduction

The hydrating† 1,8-terpin is important because of its relationship to a large group of monoterpenoids which include examples from the acyclic, monocyclic, and bicyclic series. It is obtained commercially by the addition of the elements of water‡ to naturally occurring terpenes, and by controlled dehydrohydroxylation it is converted to the terpineols used in perfumery. The easily isolated hydrate has a long history, having been obtained by Buchner in 1820.§ Brühl (1888) assigned the 1,4-dihydroxy structure I to the hydrating terpin and on the basis of this formula Baeyer (1893*b*) recognized the possibility for geometrical isomerism and prepared the isomeric terpin for the first time. Wagner (1894) corrected the structural formula of the terpins to II. However, the name *cis*-terpin used by Baeyer for the hydrating form was retained by Ginsberg (1897), who assigned to it structure IIIa, although the original structural assignment (Baeyer 1893*b*) referred to the erroneous 1,4-structure.




(I) (II) (IIIa)

An indication that Ginsberg's configuration was correct, though fortuitous, was given by the synthesis devised by W. H. Perkin Jr. (Perkin and Kay 1907).

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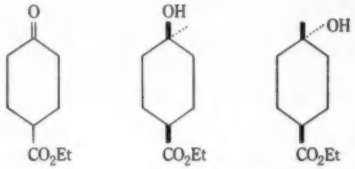
† The term "hydrate" in this paper refers only to the crystal hydrate.

‡ This chemical process is subsequently called "hydrohydroxylation" (cf. hydrochlorination etc.).

§ For historical review see Simonsen and Owen (1947).

In this, 4-ethoxycarbonyl*cyclo*hexan-1-one (IV) reacted with methylmagnesium iodide to give terpin hydrate in small yield. Previously Perkin (1904) had found the initial reaction product to be exclusively the *trans*-hydroxy ester (V),* the configuration of which was established by lactone formation of the parent acid. It seems reasonable then that the hydrating terpin should also have the *trans*-structure (IIIa) resulting from more complete reaction of V, although this inference was not drawn until the work of Pascual and Coll (1953*b*). One possible criticism is that although Perkin isolated only the *trans*-ester (V), it would be expected that the *cis*-ester (VI) would be a major product of reaction of IV with the Grignard reagent. Thus it has been shown (Barnes and Palmer 1956; Barton, Campos-Neves, and Cookson 1956; Beton *et al.* 1957) that cholestanone reacts with methylmagnesium iodide to give approximately equal quantities of the epimeric carbinols. If both hydroxy esters V and VI were formed, there is no indication from Perkin's work as to which gave rise to *trans*-terpin hydrate on further reaction.




(IV) (V) (VI)

The position was clarified by Pascual and Coll (1953*a*, 1953*b*), who isolated the two hydroxy esters V and VI from the Grignard reaction. Separate reaction of the two pure esters with methylmagnesium iodide then gave exclusively *trans*-terpin hydrate from V and *cis*-terpin from VI. It follows that the previously assigned structures (Ginsberg 1897) are correct and that the terpin formerly known as *cis*-terpin is *trans*-*p*-menthane-1,8-diol (III), and the terpin formerly known as *trans*-terpin is *cis*-*p*-menthane-1,8-diol (VII).

With the structure and configuration of the terpins definitely established, it becomes possible to critically examine other methods for their formation, their chemical transformation products, and their physical properties.

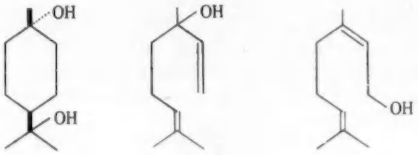
## II. Hydrohydroxylation of Olefins

*trans*-Terpin (III) is the main terpin isolated after acid treatment of linalool (VIII), geraniol (IX), nerol (X), (+)- or (−)-limonene (XI), (±)-dipentene (XI), α-pinene (XII), β-pinene (XIII), α-terpineol (XIV), and β-terpineol (XV). In the open chain compounds VIII, IX, and X, the first step is ring closure, for under mild conditions α-terpineol (XIV) is the main product, and it is always

* This ester and the derived acid have previously been called *cis*-compounds (Perkin and Kay 1907; Pascual and Coll 1953*a*, 1953*b*) because of the *cis*-relationship of functional groups. The nomenclature used in this paper refers to the carbon skeleton. Thus the previously named *cis*-terpin (IIIa) is more correctly a *trans*-compound and this systematic nomenclature is used here.

a co-product (Bouchardat 1879, 1893; Tiemann and Schmidt 1895; Stephan 1898; Zeitschel 1906. Discussion of the interesting case of the cyclization of active linalool (VIII) to active α-terpineol (XIV) is given by Ruzicka 1956). The configuration determining step in forming *trans*-terpin may therefore be regarded as occurring through α-terpineol.

With the pinenes the strained *cyclo*butane ring must be broken, and this requires protonation initially to the ion XVIa which is obtained from both α- and β-pinene. Rearrangement may then occur to give either XVIb, which leads to other bicyclic products, or with proper choice of conditions ring fission



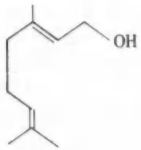
(VIIa)



(VIII)



(IX)



(X)

(XI)

(XII)

(XIII)

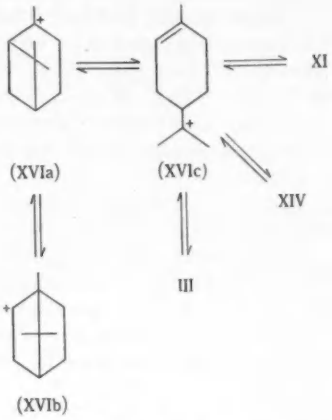
(XIVa)

(XVa)

occurs to give the monocyclic ion XVIc. This may then hydroxylate to give α-terpineol (XIV), hydrohydroxylate at the olefinic link to give a terpin, eliminate a proton to give dipentene (XI), or rearrange by 1,2-shifts of protons to give other dienes after elimination. The olefins may also yield polymers. All of these compounds are found as by-products.

Again it is seen with the pinenes, and dipentene (XI) that *trans*-terpin arises by way of α-terpineol or the equivalent ion XVIc, and the configuration determining step will be hydrohydroxylation of the cyclic double bond. Hydrohydroxylation of α-terpineol may now be considered.

The conformation of α-terpineol (or the ion XVIc) will be dictated by the necessity for the massive hydroxy*iso*propyl group to adapt an equatorial position as in XIVb. Ionic additions (and olefin forming eliminations) require a *trans*-relationship of the entering (or leaving) groups (Ingold 1953) with the added




requirement that with a cyclic compound the groups will be diaxial so as to allow a planar transition state (Barton 1953). Applying these principles to α-terpineol (XIV) and with the added directing effect predicted by the Markownikoff rule, it is seen that the terpin resulting on hydrohydroxylation (*trans*-terpin) should have the configuration and conformation shown in IIIb.

(XIVb)

(IIIb)

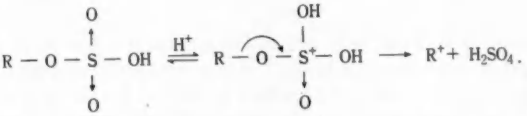
This argument requires qualification on several points. Firstly, a uniform product would result only if the predicted conformation were the only reactive species. In agreement it would be expected that the degree of conformational stability of α-terpineol would be of the same order as that of the 4-*tert.*-butyl-*cyclo*hexan-1-ol system used by Winstein and Holness (1955), and the low temperature of reaction (Aschan (1919) worked at 0 °C, while Wiggers (1840, 1846), Flawitzky (1879), and Bouchardat (1879, 1893) operated at room temperature) would not favour conformational changes. Also the introduced axial hydroxyl imposes no conformational strain, since the alternative *cis*-structure VII, has an axial methyl group.

However, despite these factors operating to stabilize the preferred conformation and to favour the production of *trans*-terpin, the single unfused ring system remains capable of conformational inversion, so that it is not surprising that some *cis*-terpin (VII) always results. Although the earlier workers isolated only

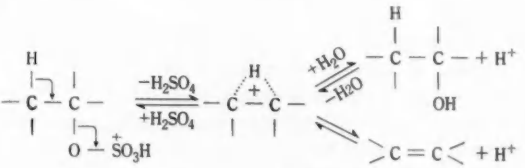
*trans*-terpin, it has been shown more recently by Lombard and Geiger (1956) that substantial quantities of *cis*-terpin are formed at 15 °C with sulphuric acid treatment of limonene or α-terpineol. Under similar reaction conditions *trans*-terpin itself was converted in part to *cis*-terpin. The fact that in each case *trans*-terpin is the major product is consistent with the above generalizations.

Secondly, rules for the stereospecific addition of ions apply only to true solutions. In agreement *trans*-terpin is obtained by acid treatment of pinene or α-terpineol in alcoholic solution (Wiggers 1840, 1846; Flawitzky 1879; Hirao and Takano 1937, 1938*a*, 1938*b*, 1938*c*). While the normal procedure using dilute aqueous acids is apparently a heterogeneous reaction, it is probable that the final hydrohydroxylation step occurs on an ion such as XVIc which is solvated at the time of reaction.

When the catalyst is dilute hydrochloric, hydriodic, nitric, sulphuric, or benzenesulphonic acids (Flawitzky 1879; Wiggers 1840, 1846; Wallach 1885; Charlton and Day 1937) it is probable that the elements of water are added directly to the double bond. With higher concentrations of sulphuric acid (Lombard and Geiger 1956) it is likely that the sulphate ester of *trans*-terpin is the initial product, from which *trans*-terpin is formed on hydrolysis. Because of the strong polarity of the coordinate links the ester hydrolysis would involve alkyl-oxygen fission:



Then the carbonium ion formed must be hydroxylated with retention of configuration, or racemization with some inversion would occur to give predominantly *cis*-terpin. This retention can be achieved by participation of the neighbouring axial hydrogen:

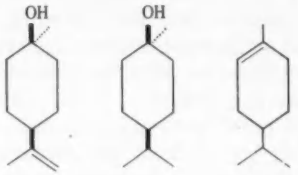


Again elimination may occur to give olefins, which are usual by-products.

When β-terpineol ((XV), Stephan and Helle 1902) was hydrohydroxylated directly with sulphuric acid (Wallach 1908*b*) or after intermediate formation of a chloro-compound (Wallach 1906) *trans*-terpin was the only terpin isolated. Since the olefinic link is in a side chain the configuration of the starting material must be analogous to *trans*-terpin, that is, β-terpineol is *trans*-1-hydroxy-*p*-menth-8(9)-ene (XVb).

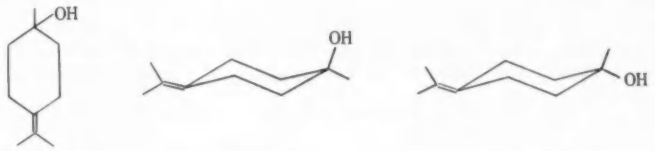
β-Terpineol is hydrogenated (Wallach 1908*c*, 1911) to a *p*-menthan-1-ol which must be the *trans*-compound (XVI). This has been prepared by Baeyer (1893*a*) by hydrohydroxylation of *p*-menth-1-ene (XVII).

The position with γ-terpineol (XVIIIa) is different from any of the examples so far discussed. Here the trigonal carbon atom destroys asymmetry and the two possible conformations XVIIIb and XVIIIc would have approximately




(XVb) (XVI) (XVII)

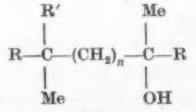
equivalent energies, so that hydrohydroxylation would give both terpins in equivalent amounts. In agreement, Wallach (1907*c*, 1908*b*) has shown this to be the only terpineol giving significant quantities of *cis*-terpin on hydrohydroxylation.




(XVIIIa) (XVIIIb) (XVIIIc)

## III. The Crystal Hydrates

The most striking difference between *cis*- and *trans*-terpin is in the ease with which *trans*-terpin forms hydrated crystals while *cis*-terpin remains anhydrous. In his review of the hydrating alcohols, Hatt (1956) discussed the structures of the known alcohol hydrates. Particularly for some of the aliphatic alcohols and diols the analysis was successful in indicating preferred structures for hydrate formation as well as the crystal structure. Thus for the closely analogous series pentamethyl ethanol (XIX ; R=R′=Me ; *n*=zero), *meso*butan-2,3-diol (XIX ; R=H ; R′=OH ; *n*=zero), and pinacol (XIX ; R=Me ; R′=OH ; *n*=zero), the hydrate crystal was regarded as being composed of a collection of spiralling threads of the alcohol bonded by water molecules. When the glycol is a cyclic vicinal glycol the analogy to pinacol is again obvious.




(XIX)

So that hydration could occur it was suggested that " spatial factors are all important ", and the further important observation was made that in the case

of the glycols the hydroxy groups must be fully repelled. By extending these ideas it may now be possible to increase the usefulness of hydrate formation as a diagnostic tool. This is done by extending the analogy to include non-vicinal diols.

When the hydrating cyclic vicinal diols are considered, it is seen that the hydroxyls are always axial and project at right angles to the plane of the ring. Furthermore it is seen that when the fully staggered structural formulae, having the hydroxyls repelled, of a polymethylene glycol (e.g. XIX ; R′=OH ; $n$=2) and a hydroxy-substituted *cyclo*hexane are projected as in Figure 1, that only the quasiaxial and axial hydroxyls bear this relationship to the hydrocarbon mass. It seems probable that this may be a necessary feature to allow a suitable shape for crystal packing in the hydrate, and the hypothesis is made that: *when an analogy exists between the structure of a polymethylene glycol or a cyclic alcohol and pinacol* (or pentamethyl ethanol), *hydration will occur only if the hydroxy group is quasiaxial or axial.*

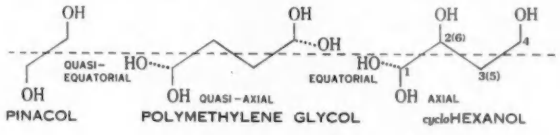



Fig. 1.—Projection formulae of alcohols.

For polymethylene glycols (XIX ; R′=OH) where $n$ is an odd number, some distortion of the chain is necessary to allow the correct alignment of the hydroxyls with the carbon chain. Where $n$=1, steric forces are prohibitive and no hydrate is formed, but for larger odd numbers for $n$, the distortion is spread along a greater chain length and the lesser repulsive interactions need not prohibit hydration.

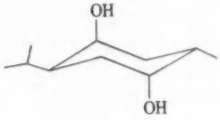
Because other less well-defined spatial factors may operate, the hypothesis only predicts which structures within a series may hydrate. Thus given a hydrating isomer in a pair of epimeric alcohols where conformations may be assigned, or two possible conformations for a symmetrical alcohol, it will predict which one will hydrate. For the symmetrical polymethylene glycols and *cyclo*hexane-1,4-diols (cf. Hatt 1956) the conformation of the alcohol in the hydrate cannot be shown by chemical means. For *cyclo*hexane-1,4-diol itself, thermodynamic factors favour the diequatorial form, however, when two larger alkyl groups are so placed equatorially as to force the hydroxyls into a *trans*-diaxial arrangement as in *p*-menthane-2,5-diol (XX) (Blumann and Ryder 1949), hydration may and does occur.

Again of the 4-*iso*propyl*cyclo*hexanols only one isomer hydrates. The *cis*-configuration assigned (Cooke, Gillespie, and Macbeth 1939) to this compound is in agreement with its method of formation, its physical properties, and on the basis of the expected conformation XXI, to its hydrating properties.

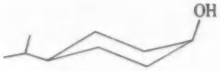
In practice, the hypothesis seems to apply to the simpler cyclic alcohols, though a possible exception is *cis*-decalin-9,10-diol (XXII). However, here

there is ambiguity with respect to the conformations of the hydroxyls, and as previously stated (Hatt 1956) this hydrate " may have an entirely different type of structure ".

The *p*-menthane-2,8-diols (Schmidt 1950, 1955) present examples closely analogous to glycols of the type XIX (R′=OH ; $n$=2) and it would be expected that the hydrating form would have the configuration XXIII or XXIV, in disagreement with that previously assigned (Schmidt 1955 ; Hatt 1956). As

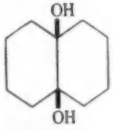



(XX)

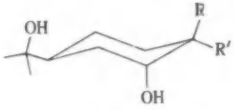



(XXI)

pointed out (Hatt 1956), the evidence concerning these structures is confused, but on the basis of the relative saponification rates of the esters of the sobrerols and carveols, and by application of the revised (Kelly 1957) Auwers-Skita rule to the latter, it is likely that the accepted configurations of these compounds should be reversed. If this is so the hydrating menthane-2,8-diol is derived from *trans*-sobrerol and has a structure in agreement with that predicted above.

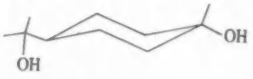



(XXII)

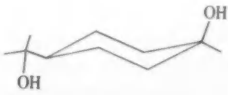



(XXIII: R = H, R′ = Me)
(XXIV: R = Me, R′ = H)

The 1,8-terpins are analogous to the glycols (XIX ; R′=OH ; $n$=3) and some distortion is necessary to achieve the shape required for hydration. Although the *cis*-structure VII has been preferred (Hatt 1956) for the hydrating terpin on the basis of the conformation VIIb, it is rendered improbable since distortion to the required form necessitates a half-boat ring with a maximum energy content. On the other hand, deformation of the *trans*-form with an axial hydroxyl (IIIb) need be comparatively slight to allow hydration on the hypothesis above. Again chemical facts are in agreement.




(VIIb)

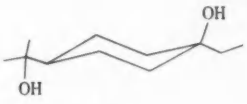



(IIIb)

Analogous to the terpins is homoterpin (Wallach 1907*b*) and the hydrating form may now be assigned the *trans*-configuration (XXV).

Homoterpin has been prepared by hydrolysis of ethylnopinol (see below) and by hydrohydroxylation (Wallach 1908*a*, 1917) of the isomers XXVI and

XXVII. These last two methods are similar to the preparation of terpin hydrate from α-terpineol, so the expected structure for homoterpin is *trans*-1-ethyl-4-(2-hydroxypropan-2-yl)*cyclo*hexan-1-ol (XXV) in agreement with the hydration evidence.

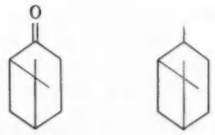



(XXV)

(XXVI; R = H, R′ = OH)
(XXVII; R = OH, R′ = H)

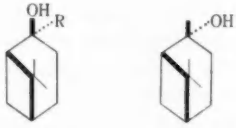
## IV. Reactions of Nopinone

Nopinone (XXVIII) reacts with methylmagnesium iodide to give a methylnopinol (pinan-2-ol,* m.p. 59 °C) (Wallach 1907*a*). The epimeric methylnopinol (m.p. 79 °C) was prepared by permanganate oxidation (Lipp 1923) or autoxidation (Fisher, Stinson, and Goldblatt 1953) of pinane (XXIX). Both methylnopinols give terpin hydrate on acid treatment.




(XXVIII) (XXIX)

By applying the Cram rule of Asymmetric Induction, Fisher, Stimson, and Goldblatt (1953) assigned the *trans*-structure (XXXa ; R=Me) to the Grignard product (m.p. 59 °C) and by consideration of other steric effects, the *cis*-structure XXXIa to the epimer (m.p. 79 °C).




(XXXa) (XXXIa)

By the action of ethylmagnesium iodide on nopinone, Wallach (1907*b*) prepared an ethylnopinol which by analogy may be given the *trans*-structure (XXX ; R=Et). On acid treatment this gave homoterpin hydrate.

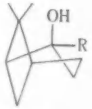
* Numbering as recommended by the Nomenclature Committee of the Division of Organic Chemistry, American Chemical Society (1955), see " System of Nomenclature for Terpene Hydrocarbons " (American Chemical Society : Easton, Pa.).

It is seen then that no matter what the configuration of the alkylnopinols, the acid treatment product, which is formally derived only by fission of the *cyclo*butane ring, has the same configuration in each case. This is easily explained by consideration of possible reaction paths (cf. Hückel 1943).

With the *trans*-alkylnopinols (XXX) two conformations XXXb and XXXc (R=Me or R=Et) are possible and neither seems to be preferred. In the first of these (XXXb) the hydroxy group is unsuitably placed for elimination and reaction must occur through the alternative conformation (XXXc) which has an axial hydroxyl. Elimination then gives an olefin, which may hydrate in the same way as α-pinene. Therefore, the terpin or homoterpin produced will have the *trans*-configuration as previously deduced.

With *cis*-methylnopinol (XXXI) the hydroxy group of the conformation XXXIb is coplanar with $C_1$, $C_2$, and $C_6$, so that on protonation a displacement may occur (cf. dehydration of lanosterol, Barton 1953) to give the ion XVIc which may hydroxylate to give α-terpineol or hydrate to *trans*-terpin as previously. Support for this mechanism comes from the observation of Wallach (1908*a*) that α-terpineol may be the main reaction product.

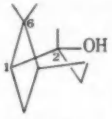
(XXXb)



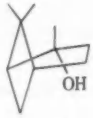

(XXXc)

Alternatively, the conformation XXXIc with an axial hydroxyl may initially dehydrohydroxylate to α-pinene (XII) which hydrohydroxylates and hydrolyses as previously discussed, again to *cis*-terpin.

It is seen that the configuration of the product at $C_1$ bears no relationship to the configuration at the same centre in the starting material.




(XXXIb)




(XXXIc)

## V. The 1,8-Dihalogeno-*p*-Menthanes

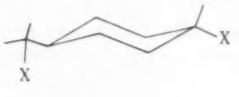
Each of the isomeric dibromo-, dichloro-, and di-iodo-*p*-menthanes is known, and the history of their configurational assignments is similar to that of the terpins. Thus Baeyer (1893*b*) assigned *cis*- and *trans*-structures on the basis of the physical properties of the dibromo compounds, but with respect to the erroneous 1,4-disubstituted structure as in I. The names have remained in use, even though the structures have been corrected.

Examination of the expected conformations for the *cis*- and *trans*-isomers shows that the *cis*-form (XXXII: X=halogen) has both large substituents

in the stable equatorial position (XXXIIb) while the *trans*-form (XXXIII; X=halogen) must always have one large group in an axial position tending towards destabilization (XXXIIIb and XXXIIIc). In agreement, one member of each dihalogen pair has one isomer of very much greater stability than the other.

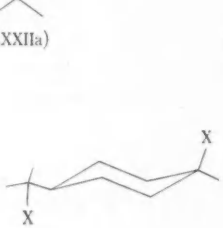
The 1,8-dibromo-*p*-menthanes (dipentene or limonene dihydrobromides) have the more stable form with m.p. 64 °C and called *trans* by Baeyer (1893*b*). It is the sole or main product from addition of hydrogen bromide at elevated temperatures to limonene, dipentene, terpinolene or pinene (Wallach 1887), or to 1-bromomenth-4(8)-ene (Baeyer 1895) or by addition and substitution to α-, β-, or γ-terpineol (Baeyer 1894; Wallach 1887, 1906) or cineole (Wallach

(XXXIIa)

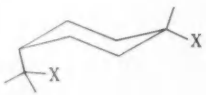



(XXXIIb)

(XXXIIIa)




(XXXIIIb)




(XXXIIIc)

1887); or by substitution with *cis*- or *trans*-terpin (Baeyer 1893*b*; Wallach 1887). In these warm reactions equilibrating conditions prevail and the product, m.p. 64 °C, is undoubtedly the thermodynamically more stable *cis*-1,8-dibromo-*p*-menthane (XXXII; X=Br). Barton, Campos-Neves, and Cookson (1956) have shown that hydrogen halides may add to olefins to give the more stable product, even though this is not obtained by *trans*-diaxial addition.

The isomeric bromide, m.p. 40 °C, is obtained with difficulty and forms the main yield only when cineole is treated with hydrogen bromide at low temperatures (Baeyer 1893*b*). This must be the less stable *trans*-1,8-dibromo-*p*-menthane (XXXIII; X=Br).

The more stable dibromide (m.p. 64 °C) shown to have an equatorial bromine atom (XXXII; X=Br) gives *cis*-terpin (VII) exclusively on treatment with silver acetate in acetic acid (Baeyer 1893*b*). This was the first stereospecific synthesis of *cis*-terpin and it involves retention of configuration at $C_1$. A bimolecular displacement which would involve inversion is precluded by the shielding effect of the ring (Bartlett and Rosen 1942) so that the retention is analogous to the deamination of equatorial amines (Mills 1953). Likewise

treatment of *cis*-terpin (VII) with hydrogen bromide even in the cold gives exclusively the more stable bromide with retention (Baeyer 1893*b*), which is analogous to the formation of menthyl chloride from menthol by treatment with hydrogen chloride (Hückel and Pietrzok 1939).

The lower melting bromide (m.p. 40 °C) now assigned the *trans*-structure (XXXIII ; X=Br) has an axial bromine which is suitably placed for elimination. The reaction product on treatment with silver acetate in acetic acid (Baeyer 1893*b*) is more complex, yielding *trans*-terpin (III) and elimination products. The terpin is again formed by retention of configuration, possibly due to the influence of neighbouring group participation as in the hydrolysis of the sulphate esters.

The formation and reactions of the 1,8-dichloro-*p*-menthanes (dipentene or limonene dihydrochlorides) are analogous to the corresponding bromides. Thus the more stable form (m.p. 50 °C) is found as major product from the action of hydrogen chloride on a variety of monoterpenoids (Tilden 1879 ; Wallach 1884, 1885, 1887, 1888, 1906, 1907*a*, 1908*c*). This has been given the *trans*-structure by Baeyer (1893*b*) but is now assigned the *cis*-structure (XXXII ; X=Cl).

The less stable form (m.p. 25 °C) previously called *cis* (Baeyer 1893*b*) is now assigned the *trans*-structure (XXXIII ; X=Cl). It is prepared by the action of hydrogen chloride on cold cineole.

The hydrolysis of the dichlorides (Wallach 1906) is less specific than for the dibromides, possibly because higher temperatures were used. Thus from both dichlorides were obtained dipentene (XI), terpineol (XIV), and *trans*-terpin (III). However, it is significant that *cis*-terpin (VII) was isolated only from the *cis*-dichloride (XXXII ; X=Cl) (cf. the reaction of the *cis*-dibromide above). More recently Lombard and Geiger (1953) have shown *cis*-terpin to be produced in five times the amount of *trans*-terpin on treatment of the stable dichloride with silver oxide in water.

By analogy, the 1,8-di-iodo-*p*-menthanes (Wallach 1885, 1887, 1894) may have the *cis*-structure (XXXII ; X=I) assigned to the more stable form of m.p. 77 °C and the *trans*-structure (XXXIII ; X=I) to the lower melting form (m.p. 50 °C).

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# THE APPEARANCE OF POLAR FORMS OF 1,4–DIOXAN AT TEMPERATURES ABOVE 200 °C

By R. S. Armstrong,* R. J. W. Le Fèvre,* and J. Yates*

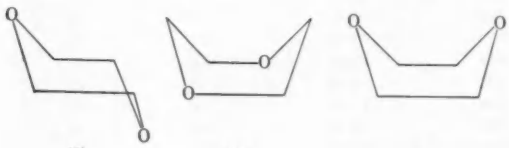
[*Manuscript received August* 19, 1957]

*Summary*

The total polarization of 1,4-dioxan vapour is reported for 20 temperatures between 118 and 365 °C. The results, considered together with 19 others previously recorded over a range down to 56 °C, indicate the generation of polar forms at higher temperatures, and confirm an earlier suggestion by Gibbs (1951). The variation of $P$ with $1/T$ °K is shown graphically and may also be qualitatively forecast by equations having a semi-empirical character; a steep rise of $P$ is predicted as $T$ is increased above about 200 °C.

## I. Introduction

At irregular intervals during the past few years the total polarization of dioxan vapour has been examined in these laboratories. Some of the results have already been published (Le Fèvre and Rao 1955); the purpose of the present paper is to record the remainder. Their interest lies in the fact that they reveal a tendency, with rising temperatures, for the non-polar " chair " configuration of 1,4-dioxan (I) to rearrange into polar " boat " forms, II or III.



(I) (II) (III)

They thus justify a suggestion made, on more limited experimental evidence, by Gibbs (1951, speaking for himself and Professor C. P. Smyth) at the Faraday Society discussion on " Hydrocarbons " in 1951.

## II. Measurements

Dioxan and benzene were samples purified as specified by Armstrong, Le Fèvre, and Le Fèvre (1957). The apparatus employed initially was the Franklin oscillator-wavemeter combination of Le Fèvre, Ross, and Smythe (1950); modifications enabling the use of higher temperatures were later introduced; these have been noted by Freeman *et al.* (1955). Practical procedures and methods of calculation follow those described by Le Fèvre (1953). Benzene has been adopted as a standardizing vapour, its polarization being taken for

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this purpose as 27·0 c.c. from Le Fèvre and Rao (1955), and earlier measurements based upon ${}_TP_{\text{benzene}}=26·62$ c.c. (Buckingham, Holland, and Le Fèvre 1954) have been adjusted appropriately before inclusion in Table 1, which summarizes our unpublished results.

Regarding the third column of Table 1 it should be explained that an "observation" involves in fact four operations: firstly, the mean is taken of two capacity changes, $\delta C_1$, determined when the initially evacuated dielectric cell is filled with dioxan to a pressure $p$ cm, and $\delta C_2$, noted subsequently on re-evacuation; secondly, a corresponding set of $\delta C$'s must also be found for the

TABLE 1

TOTAL POLARIZATIONS OF DIOXAN AT VARIOUS TEMPERATURES

| Temperature of Observations (°K) | Pressure Range of Observations (cm Hg) | Number of Observations | ${}_TP$ (c.c.) |
|---|---|---|---|
| 391 | 10–15 | 14 | 24·5±0·3 |
| 399 | 12–21 | 10 | 24·2±0·3 |
| 402 | 10–30 | 8 | 24·6±0·3 |
| 424 | 16–49 | 12 | 23·5±1·3 |
| 430 | 11–30 | 10 | 24·3±0·3 |
| 460 | 10–28 | 10 | 24·6±0·4 |
| 485 | 11–22 | 10 | 26 ±1 |
| 511 | 12–23 | 11 | 25 ±1 |
| 516 | 11–28 | 11 | 25 ±2 |
| 517 | 15–30 | 10 | 25 ±2 |
| 534 | 12–25 | 15 | 28 ±2 |
| 566 | 20–30 | 10 | 26 ±3 |
| 571 | 6–27 | 14 | 26 ±2 |
| 594 | 11–25 | 13 | 27 ±1 |
| 595 | 19–43 | 10 | 29 ±2 |
| 596 | 14–34 | 11 | 30 ±3 |
| 602 | 16–34 | 10 | 31 ±4 |
| 620 | 9–32 | 10 | 28 ±3 |
| 631 | 20–37 | 10 | 29 ±2 |
| 638 | 15–41 | 10 | 27 ±3 |

standard vapour (benzene). The quotients $(\delta C_1+\delta C_2)/2p=\Delta C/p$ ascertained for the number of $p$'s stated in the third column (and for $p$'s lying within the ranges given in the second column) are then extrapolated to zero pressure. The polarization of dioxan at the listed temperature follows as $27·0(\Delta C/p)^{\text{dioxan}}_{p=0} \div (\Delta C/p)^{\text{benzene}}_{p=0}$. Through causes we could not discover or control (poor temperature equilibration within the cell was strongly suspected) the last ratios proved much less smooth versus pressure above about 500 °K than at lower temperatures. Analysis of the $\Delta C/p$ quotients actually read indicate standard deviations in $P$ as shown in Table 1.

Figure 1 shows polarization against the reciprocal of the absolute temperature and includes all the results listed in Tables 1 and 2. As suggested by Gibbs the

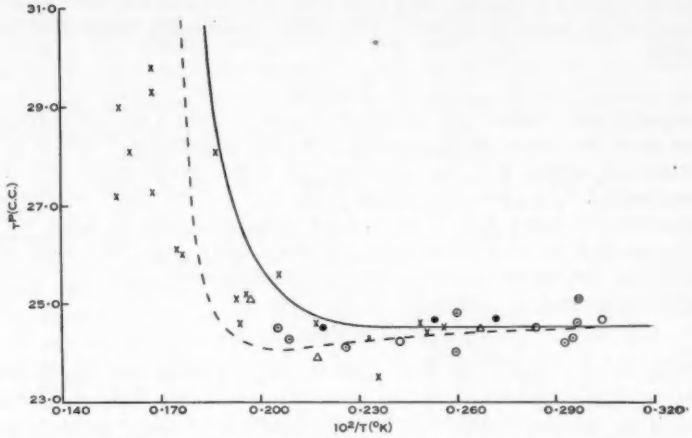


Fig. 1.—Polarization plotted against the reciprocal of the absolute temperature. △ Gibbs; ○ Kubo; ● Le Fèvre and Rao; ⊙ Schwingel and Greene; × Present work.

TABLE 2

POLARIZATIONS DETERMINED BY OTHER AUTHORS

| Temperature (°K) | Polarization (c.c.) | Author(s) |
|---|---|---|
| 337·0 | 25·1 | Schwingel and Greene (1934) |
| 337·1 | 24·6 | |
| 339·0 | 24·3 | |
| 341·2 | 24·2 | |
| 384·7 | 24·8 | |
| 385·0 | 24·8 | |
| 385·2 | 24·0 | |
| 442·0 | 24·1 | |
| 487·0 | 24·5 | |
| 328·7 | 26·39 | Kubo (1936) |
| 352·1 | 26·20 | |
| 412·4 | 25·91 | |
| 478·9 | 25·95 | |
| 375* | 24·5* | Gibbs (1951) |
| 461* | 23·9* | |
| 507* | 25·1* | |
| 368 | 24·7 | Le Fèvre and Rao (1955) |
| 396 | 24·65 | |
| 456·5 | 24·5 | |

* Read from graph of $P$ *v.* $1/T$ shown by Gibbs (1951).

values recorded by Kubo have been lowered by 6·5 per cent. for plotting purposes, an inaccurately determined cell constant being presumably responsible for their largeness.

## III. Discussion

Despite their scatter, the points in Figure 1 lie in a curved corridor and clearly show that some fairly powerful relationship between $P$ and $T$ becomes important at about 480 °K; although at lower temperatures $P$ is either independent of $T$ or varies only slightly with $1/T$. (The mean polarization for 23 temperatures below 480 °K is $24 \cdot 4_4$ c.c. compared with $24 \cdot 4_8$ c.c. for eight points recorded by Schwingel and Greene (1934) over the same range.) Empirically, the values observed for $P$ at temperatures *above* 520 °K can be roughly represented by equations of the form

$$P_T = 24 \cdot 4 \exp [(T - 520)/520].$$

Theoretically there are five possible configurations for the 1,4-dioxan molecule. These are: (1) a planar form with symmetry $D_{2h}$, (2) a "chair" or *trans*-form with symmetry $C_{2h}$, (3) a symmetrical "boat" or *cis*-form with symmetry $C_{2V}$, (4) an unsymmetrical "boat" or *cis*-form with symmetry $C_2$, or (5) an irregular form with no symmetry elements. Formulae I, II, and III indicate respectively the "chair", unsymmetrical "boat", and symmetrical "boat" structures.

Experimental evidence in the matter comes from several sources. The polarity of dioxan in solution has been examined by Sangewald and Weissberger (1929), Williams (1930), Smyth and Walls (1931), Hunter and Partington (1933), and Boeseken, Tellegen, and Henriquez (1935), who reported moments indistinguishable from zero by the methods used. More recent measurements by Vaughan (1939) and Yasumi and Shirai (1955) on liquid dioxan confirm that at temperatures below 70 °C the molecule has no permanent dipole moment and must therefore exist as either form (1) or form (2), or as an equilibrium between (1) and (2). Dielectric polarizations of dioxan vapour have been taken at temperatures above 70 °C by Schwingel and Greene (1934), Kubo (1936), Le Fèvre and Rao (1955), and Gibbs (1951), but, except for results of the last author, no definite indications emerged of a polarity increase with temperature.

Kohlrausch and Stockmair (1935) investigated the Raman spectrum of liquid dioxan and concluded that form (2) was very probable on the grounds that the 17 Raman displacements observed were only one short of the number (18) expected for the *trans*-form, whereas the symmetrical and unsymmetrical *cis*-structures should both have produced more because of their lower degrees of symmetry. However, other workers have differed somewhat from Kohlrausch and Stockmair: Villars (1930) listed 10 displacements, Volkenshtein and Syrkin (1935) 11, Simon and Feher (1936) 16, and Venkateswaran (1935) 24. Nevertheless, Ramsay (1947), Burket and Badger (1950), and Malherbe and Bernstein (1952), from considerations of *both* Raman and infra-red spectra, find no evidence to suggest that form (3) is present in other than "an almost negligible amount".

Sutton and Brockway (1935) studied the electron diffraction of dioxan. Assuming reasonable values for the bond distances and valency angles (C—O,

1·46 A, C—C, 1·51 A, ∠C—C—O, 109·5°, ∠C—O—C, 110°) they showed that the intensity curve can best be understood by assigning to dioxan the *trans*-configuration (2). Similar investigations by Hassel and Viervoll (1947) and Kimura and Aoki (1951) have supported the Sutton-Brockway viewpoint.

The results of Gibbs (1951) and those of the present paper, therefore, appear to be the first cases in which the intervention of polar " boat " forms is indicated by experiment. Gibbs proceeds to discuss the situation thus : the polarization may be expressed as a function of temperature, in terms of the dipole moments and energies of the various forms, by means of the Boltzmann distribution law, and, since the moment of each form may be roughly calculated by vector addition of the various link moments, an expression for the mean square moment $\overline{\mu}^2$, involving the energies of the symmetrical and unsymmetrical *cis*-structures, can be obtained ; $\overline{\mu}^2$, when substituted into the Clausius-Mossotti-Debye relation, should give an equation for the experimentally determined curve. Gibbs finds a close approach to a fit only if the orders of the energies of the forms is :

$$E_{\text{sym. } cis} > E_{\text{unsym. } cis} > E_{trans}.$$

## IV. Equations to Represent Polarization Against Reciprocal Temperature

During the present work two equations for $P_{\text{obs.}}$ *v.* $1/T$ have been evolved. For the first of these the relation (1), written by Meyer (1930) and also used by Sturtevant (1933), has been adopted (since intuitively the *cis-trans* dioxan equilibria is a case involving " restricted " rotations about single bonds (cf. Le Fèvre 1953, pp. 118–31).

$$_{o}P=\frac{4\pi N}{3}\left[\frac{2\overline{\mu}^2 \sin^2\theta}{3kT}(1-x)\right]. \quad \ldots\ldots\ldots\ldots (1)$$

In (1) $_{o}P$ is the orientation polarization, and $x$ is given by (2)

$$x=\frac{\alpha/kT+\beta/(kT)^2+\gamma/(kT)^3}{m+n/kT+o/(kT)^2}. \quad \ldots\ldots\ldots\ldots (2)$$

In the case of dioxan the following approximations may be made

$$\alpha/kT+\beta/(k/T)^2+\gamma/(kT)^3 \doteqdot a+b[(1/T)+y]+c[(1/T)+y]^2+\exp[g-(F/T)],$$

and

$$m+n/kT+o/(kT)^2=a+1/[(1/T)+y]+1/[(1/T)+y]^2.$$

Insertion of empirical constants then gives (3)

$$_{o}P=2\cdot5T_R\frac{-0\cdot101+1\cdot36T_R^2+10^{-4}/\exp(143\cdot0T_r-33\cdot61)}{-0\cdot101+0\cdot582T_R+T_R^2}. \quad .. (3)$$

in which $T_R=T_r-0\cdot015$ and $T_r$ is $10^2/T$. After adding the constant value of the molecular refraction of dioxan, (3) yields the broken curve plotted in Figure 1.

A second equation has been developed by attempting to estimate the energy of each form and using the data so obtained in an expression of the form (4), which is essentially that cited by Gibbs and Smyth (1951)

$$\bar{\mu}^2=(N_{sc}\mu_{sc}^2+2N_{uc}\mu_{uc}^2)/(N_{sc}+2N_{uc}+N_{trans}), \quad \ldots\ldots\ldots \quad (4)$$

where $N_{sc}$, $N_{uc}$, $\mu_{sc}$, and $\mu_{uc}$ are the numbers and moments of the symmetrical and unsymmetrical *cis*-forms; $N_{trans}$ is the number of *trans*-forms. Strictly the ratio $N_{sc}/N_{uc}$ is given by (5), if $f_{sc}$ and $f_{uc}$ are the appropriate partition functions:

$$N_{sc}/N_{uc}=(f_{sc}/f_{uc})\exp(-\Delta E/kT), \quad \ldots\ldots\ldots \quad (5)$$

but, following Gibbs (1951), we assume that vibrational and rotational factors in the $f$'s for the various species are the same, and the $E$'s are referred to $E_{trans}$ as zero. Therefore, only steric and dipole-dipole interactions have to be considered. For the former, expressions due to Barton (1948), Turner (1952), or Aston *et al.* (1944) are available; that (6) due to Turner is most simple and has therefore been used:

$$E_r=\Sigma kr_{ij}^{-5}. \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

(The quantities $r_{ij}$ are the distances between all the nuclei in the molecule not bonded together; in dioxan the H . . . H and O . . . O interactions are considered the most important.) The shape of each configuration was adjusted to give minimum repulsive interaction, combined with bond angles and lengths as close as possible to those listed by Stuart (1935) and Sutton and Brockway (1935); the $r_{ij}$ values were calculated by trigonometry. Dipole-dipole interactions were estimated using (7).

$$U=(1-3\cos\alpha_1\cos\alpha_2)\mu_1\mu_2/r^3, \quad \ldots\ldots\ldots\ldots \quad (7)$$

in which $\alpha_1$ and $\alpha_2$ are the angles made by moments $\mu_1$ and $\mu_2$. The total energy of each form is therefore,

$$E=\Sigma kr_{ih}^{-5}+U,$$

whence: ($k$ being empirically taken as $2\cdot41\times10^6$)

$$E_{\text{sym. }cis}=189\cdot8\times10^{-14}\text{ erg molecule}^{-1},$$
$$E_{\text{unsym. }cis}=134\cdot7\times10^{-14}.$$

The molecular resultants $\mu_{sc}^2$ and $\mu_{uc}^2$, estimated from link values, are

$$\mu_{sc}^2=3\cdot61\text{ D and }\mu_{uc}=1\cdot43\text{ D}.$$

The expected orientation polarization can then be calculated from (4) and (5) as $4\pi N\mu^2/9kT$, which with ${}_DP=24\cdot5$ c.c. yields

$$P=24\cdot5+\frac{3\cdot05\times10^{-7}}{T}\cdot\frac{3\cdot61\exp(-137\cdot5\times10^2/T)+1\cdot43\exp(-97\cdot6\times10^2/T)}{\exp(-137\cdot5\times10^2/T)+2\exp(97\cdot6\times10^2/T)+1}.$$

This equation is shown as a continuous line on Figure 1.

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# THE RADIATION CHEMISTRY OF AQUEOUS SOLUTIONS OF [$^{14}$C]BENZOIC AND [$^{14}$C]SALICYLIC ACIDS

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*Summary*

Radioactive tracer techniques have been used to study the effect of ionizing radiation ($^{60}$Co $\gamma$-radiation and 45 kV X-rays) on [$^{14}$C]benzoic acid (both carboxyl- and uniformly-labelled) and on [*carboxy*-$^{14}$C]salicylic acid in aerated aqueous solutions.

The production of *o*-, *m*-, and *p*-hydroxybenzoic acids from benzoic acid (Loebl, Stein, and Weiss 1951) has been confirmed. The approximate initial G values for these products were: *ortho*, 0·74; *meta*, 0·42; *para*, 0·33. The ratio $o:m:p$ was thus approximately 9 : 5 : 4 whereas Loebl, Stein, and Weiss found the corresponding ratio to be 5 : 2 : 10. Benzoic acid and sodium benzoate were also decarboxylated [$G(CO_2) : 0{\cdot}73 \pm 0{\cdot}03$]. The extent of decarboxylation was independent of the initial concentration of benzoic acid in the range studied ($0{\cdot}5$–$7{\cdot}0 \times 10^{-3}$M). The total reaction of the benzoic acid corresponded to a G value of approximately 2·6. Very little, if any, diphenyl was produced.

The main non-volatile products from salicylic acid were 2,3- and 2,5-dihydroxybenzoic acids which were obtained in the ratio 2,5 : 2,3 :: 1 : 1·6. The 2,4- and 2,6-isomers were not detected. Salicylic acid was also decarboxylated, $G(CO_2)$ being $1{\cdot}53 \pm 0{\cdot}07$ in alkaline solutions.

The above results are compared with other results relating to free-radical reactions. The possible use of the decarboxylation of sodium [*carboxy*-$^{14}$C]benzoate as a sensitive dosimeter for ionizing radiation is suggested.

## I. Introduction

Loebl, Stein, and Weiss (1951) studied the irradiation of saturated aqueous solutions of benzoic acid with 200 kV X-rays. They identified *o*-, *m*-, and *p*-hydroxybenzoic acids, and diphenyl as reaction products. In oxygenated solutions $o:m:p$ was approximately 5 : 2 : 10, and under virtually oxygen-free conditions the ratio was 6 : 4 : 10. The amount of salicylic acid was proportional to the dose in the presence of oxygen up to $5 \times 10^4$ Energy Units (E.U.). These authors also reviewed earlier qualitative work on the action of ionizing radiation and of free radicals on aqueous benzoic acid.

Day and Stein (1949) had previously suggested using the hydroxylation of benzene or of sodium benzoate in aqueous solution as dosimeters for ionizing radiation. Solutions irradiated in the presence of air gave phenol or sodium salicylate respectively with a yield directly proportional to the dose up to about $6 \times 10^4$ E.U., after which the reaction proceeded with decreased yield in the virtual absence of oxygen.

Other workers, using radioactive tracer methods, have shown that irradiation by 3 MeV cathode rays of aqueous solutions of nicotinic acid and of *o*- and *p*-

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aminobenzoic acids produces decarboxylation and ring cleavage (Goldblith *et al.* 1949; Corson *et al.* 1951).

There does not appear to be any previously published information on the radiation chemistry of salicylic acid.

Farmer, Stein, and Weiss (1949) recognized the difficulty of obtaining a complete analysis of the products formed by the action of ionizing radiation on organic compounds in aqueous solution, especially if the oxygen "break" (Day and Stein 1949) is not to be passed. Thus Loebl, Stein, and Weiss (1951) had to extract 1200 ml of aqueous benzoic acid which had been irradiated with $5 \times 10^4$ E.U. in order to obtain sufficient material for their paper chromatographic analyses.

This paper describes some results obtained by irradiating aqueous aerated solutions of $^{14}$C-labelled benzoic and salicylic acids with $^{60}$Co $\gamma$-radiation and 45 kV X-rays. By using radioactive tracer techniques a few microlitres of an irradiated solution could be applied directly to a strip of chromatography paper and the products detected easily on the developed chromatogram.

The original aim of this work was to study quantitatively orientation in radiation-induced reactions of simple aromatic compounds in various solvents. Since it has not been possible to continue these studies the preliminary results that were obtained are presented here.

## II. Experimental

### (*a*) *Materials*

[*Carboxy*-$^{14}$C]benzoic acid (0·462 mc/mMole) was prepared by reacting phenyl magnesium bromide with [$^{14}$C]carbon dioxide (Calvin *et al.* 1949). [$^{14}C_7$]Benzoic acid (1·0 mc/mMole; uniformly labelled) was obtained from the Radiochemical Centre, Amersham, England. [*Carboxy*-$^{14}$C]salicylic acid (0·793 mc/mMole) was prepared from sodium phenate and [$^{14}$C]carbon dioxide using essentially the method of Mandel and Smith (1950). The purity of these labelled compounds was checked by paper chromatography as described below.

The non-radioactive acids, except 2,3-dihydroxybenzoic acid, were obtained from commercial sources. 2,3-Dihydroxybenzoic acid (m.p. uncorr. 203–204 °C; lit. 204, 206 °C) was prepared by demethylating (with hydriodic acid) 2-hydroxy-3-methoxybenzoic acid which was prepared from *o*-vanillin by the method of Rupp and Linck (1915).

Solutions to be irradiated were prepared using water which had been distilled three times, the final distillation being from alkaline potassium permanganate in an all-glass apparatus. The triple-distilled water was allowed to equilibrate with air.

### (*b*) *Irradiations*

In most of the experiments a $^{60}$Co source of about 400 mc strength was used. The experimental arrangement was similar to that described by Miller and Wilkinson (1952) except that an aluminium sample holder surrounded by lead 4 in. thick was used. The source was about 18 mm from the centre of each sample and the dose rate about 23 rad/min. As the main purpose of the work was to study the relative amounts of the products formed the apparatus was

constructed very simply without trying to achieve highly reproducible dose rates. Nevertheless the doses received by the samples in the six positions were the same within ±15 per cent.

In a few experiments samples were irradiated in small open Pyrex beakers with 45 kV X-rays (20 mA; 0·12 mm aluminium absorber; 0·11 mm half-value layer) at a dose rate of 514 rad/min. A Machlett A.E.G. 50 X-ray tube with a window of 1 mm of beryllium was used.

The ferrous sulphate method of dosimetry was used (Miller and Wilkinson 1952), based on a G value of 15·6 (Farmer, Rigg, and Weiss 1955), for ferric ion production. After the initial calibration the dose rate was corrected for $^{60}Co$ decay (half-life 5·2 years).

### (c) "*Carrier*" *Dilution Analyses*

All analyses were carried out in duplicate.

(i) [$^{14}C$]*Carbonate.*—The sample to be analysed was thoroughly mixed with an aqueous solution of $Na_2CO_3$ (5 ml; 0·2074N). Carbon dioxide was then liberated by the addition of HCl and was carried by $CO_2$-free $N_2$ into a hot, saturated solution of $Ba(OH)_2$ (15 ml). The filtered $BaCO_3$ samples were counted at infinite thickness. $CO_2$ generated in this way from unirradiated solutions of the labelled benzoic or salicylic acids gave background counting rates.

(ii) [$^{14}C$]*Organic Acids.*—The sample was thoroughly mixed with an accurately weighed quantity (200–500 mg) of the appropriate carrier acid in ethanol. To measure the total $^{14}C$, an aliquot of the solution was evaporated to dryness, ground to a fine powder, and several samples counted in polythene disks at infinite thickness (Popják and Beeckmans 1950). To measure the amount of $^{14}C$ present in the form of the carrier acid concerned, the sample was recrystallized from water or aqueous alcohol until a constant counting rate was obtained. With benzoic and salicylic acids this was usually achieved after three or four recrystallizations but when analysing for $^{14}C$ as *m*- or *p*-hydroxybenzoic acids in the presence of a large amount of unchanged [$^{14}C$]benzoic acid a constant counting rate was not achieved even after five recrystallizations.

If $S$ is the counting rate corresponding to a specific activity of 1 μc/g, $x$, the observed counting rate, $W$, the mass (g) of carrier added, $V$, the volume (ml) of irradiated solution used, then the amount of $^{14}C$ present in the chemical form being analysed is given by $xW/SV$ (μc/ml) of irradiated solution since the mass of the labelled compound was negligible when compared with the mass of the carrier added.

### (d) *Chromatography*

Standard techniques were used with the following solvents:

(i) *n*-Butanol saturated with 5N $NH_4OH$.

(ii) *n*-Butanol–pyridine–saturated aqueous NaCl–aqueous $NH_3$ (*d*, 0·880) (4 : 8 : 5 : 3 by volume) (Loebl, Stein, and Weiss 1951).

(iii) Benzene–acetic acid–water (4 : 4 : 2 by volume) (Bray, Thorpe, and White 1950).

The $R_F$ values of the various acids are given in Table 1. Although the values for the dihydroxybenzoic acids in solvent 3 differed considerably from those recorded by Bray, Thorpe, and White (1950), the same sequence was observed.

TABLE 1

$R_F$ VALUES OF VARIOUS ORGANIC ACIDS

| Compound | $R_F$ Values (×100) | | |
|---|---|---|---|
| | Solvent 1 | Solvent 2 | Solvent 3 |
| Benzoic acid .. .. | 36 | 55 | 99 |
| Salicylic acid .. .. | 44 | 71 | 93 |
| *m*-Hydroxybenzoic acid .. | 13 | 47 | 30 |
| *p*-Hydroxybenzoic acid .. | 4 | 36 | 30 |
| Dihydroxybenzoic acid | | | |
| 2,3- .. .. .. | 20 | 74 | 30 |
| 2,4- .. .. .. | 14 | 62 | 18 |
| 2,5- .. .. .. | 24 | 43 | 12 |
| 2,6- .. .. .. | 58 | 86 | 7 |
| 3,4- .. .. .. | 16 | 40 | 4 |
| 3,5- .. .. .. | 3 | 51 | 4 |

### (*e*) *Radioactive Assay*

Solid samples were assayed with thin end-window G.M. counting tubes. The equipment was calibrated using samples of $Ba^{14}CO_3$ prepared by combusting portion of a standard [$^{14}$C]polymer reference source (obtained from the Radiochemical Centre, Amersham, England). A disk cut from one of the reference sources was used to check the sensitivity of the counting equipment. Counting rates were corrected for resolving time losses, and for the background counting rate.

Radioactivity on paper chromatograms 3–3·5 cm wide was usually measured by feeding the paper continuously between two mica-window G.M. tubes mounted face to face on a Perspex holder inside a lead castle. A slit 1 mm deep and 40 mm wide through the holder allowed Whatman No. 1 paper to pass through easily. The actual length of paper " seen " by the G.M. tubes was fixed at 5 mm by the insertion of aluminium absorbers (30 mg/cm$^2$) in which suitable windows were cut. The counting rate was recorded automatically with a ratemeter connected to a recording ammeter. The area of each peak on the chart recorder, measured by planimetry, was proportional to the amount of radioactivity on the chromatographic spot within ±10 per cent. With small amounts of radioactivity more accurate results were obtained by pulling the paper through manually and counting 5 mm sections to the desired accuracy with a scaler. A point source of $^{14}$C on Whatman No. 1 paper located in the centre of the scanned region was detected with an efficiency of about 10 per cent.

## III. Results

### (a) *Decarboxylation Studies*

Aqueous solutions of sodium benzoate and of benzoic acid were irradiated with $^{60}$Co γ-rays for various times and the amounts of [$^{14}$C]carbonate in the irradiated solutions determined (Fig. 1). The amount of decarboxylation was

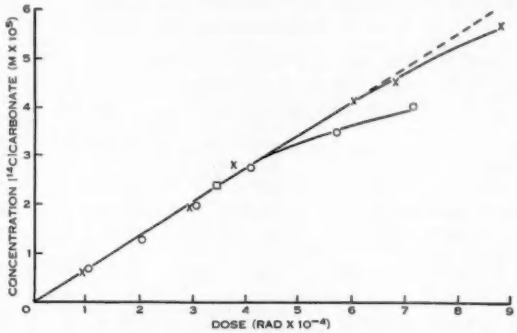


Fig. 1.—Decarboxylation of [*carboxy*-$^{14}$C]benzoic acid in aqueous aerated solutions irradiated with $^{60}$Co γ-rays.
○ Benzoic acid, $1{\cdot}3\times10^{-4}$M, pH 4; × sodium benzoate, $2{\cdot}16\times10^{-4}$M, pH 9; □ sodium benzoate, $1{\cdot}28\times10^{-4}$M, pH 9.

directly proportional to the dose until about a quarter of the benzoic acid had reacted. From Figure 1, $G(CO_2)$ for the initial stages of the reaction was calculated to be 0·66. The rate of decarboxylation was the same in acidic (pH 4) and in alkaline (pH 9) solution.

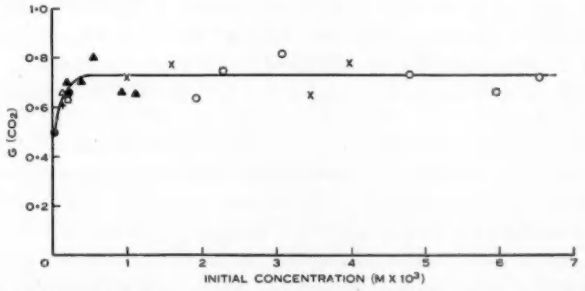


Fig. 2.—Effect of initial concentration on the decarboxylation of [*carboxy*-$^{14}$C]benzoic acid in aqueous aerated solutions irradiated with $^{60}$Co γ-rays.
+ Free acid: average of 4 samples with doses up to $4{\cdot}1\times10^{4}$ rad; ▲ free acid, $6{\cdot}2\times10^{4}$ rad; × Na salt, $6{\cdot}1\times10^{4}$ rad; ○ Na salt, $1{\cdot}4\times10^{5}$ rad; ● Na salt, average of 5 samples with doses up to $6{\cdot}9\times10^{4}$ rad; ⊙ Na salt, $9{\cdot}2\times10^{3}$ rad; □ Na salt, $2{\cdot}1\times10^{4}$ rad; △ Na salt, $3{\cdot}0\times10^{4}$ rad.

Further experiments (Fig. 2) showed that $G(CO_2)$ was independent of the initial concentration over the range $0{\cdot}5$–$7\times10^{-3}$M. The average value of $G(CO_2)$ calculated from these results was $0{\cdot}73\pm0{\cdot}03$. With initial concentra-

tions below about $0{\cdot}5\times10^{-3}$M, the amount of decarboxylation was probably lower for a given dose but insufficient values were obtained in this range to enable a complete curve to be drawn.

It is more difficult to give an accurate G value for the total change in the benzoic acid if the oxygen break is not to be exceeded. The difference between two similar, small concentrations (maximum about $1{\cdot}5\times10^{-3}$M) has to be measured unless a large proportion of the benzoic acid is allowed to react, in which case the G value obtained no longer represents the initial value. The few results obtained are shown in Figure 3, which shows that the amount of reaction fell off with initial concentrations below about $5\times10^{-4}$M. As the initial concentration was increased G(benzoic) approached a constant value of about 2·6.

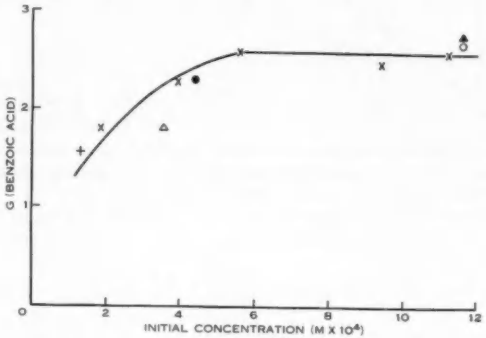


Fig. 3.—Effect of initial concentration on the total reaction of [$^{14}$C]-benzoic acid in aqueous aerated solutions irradiated with $^{60}$Co γ-rays. × [*carboxy*-$^{14}$C], $6{\cdot}2\times10^{4}$ rad; + [*carboxy*-$^{14}$C], average of 4 samples with doses up to $4{\cdot}1\times10^{4}$ rad; △ [*carboxy*-$^{14}$C], $1{\cdot}0\times10^{5}$ rad; ○ [*carboxy*-$^{14}$C], $4{\cdot}9\times10^{4}$ rad; ● uniformly-labelled, $1{\cdot}0\times10^{5}$ rad; ▲ uniformly-labelled, $4{\cdot}9\times10^{4}$ rad.

Irradiation of aqueous Na salicylate produced results similar to those obtained with benzoic acid except that $G(CO_2)$ was $1{\cdot}53\pm0{\cdot}07$ (mean of 12 results). The decarboxylation of salicylic acid was studied only in alkaline solution.

In another experiment two series of solutions, each containing a constant initial concentration of Na [*carboxy*-$^{14}$C]salicylate and various initial concentrations of non-radioactive Na benzoate, were irradiated with the same dose of $^{60}$Co γ-radiation ($1{\cdot}2\times10^{5}$ rad). The concentration of [$^{14}$C]carbonate in the irradiated solutions was measured. The results (Fig. 4) can be interpreted on the basis of a competition between the two solutes, with approximately the same G(total) values, for the free radicals produced by the action of the radiation on the water.

### (*b*) *Identification of Hydroxylation Products*

The presence of the three monohydroxybenzoic acids in solutions of irradiated aqueous [$^{14}$C]benzoic acid solutions (Loebl, Stein, and Weiss 1951) was confirmed

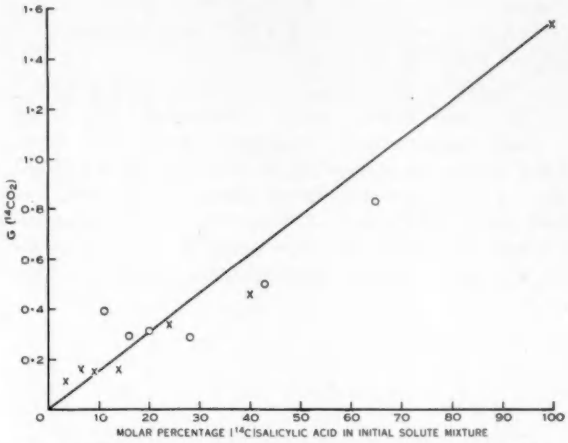


Fig. 4.—Effect of addition of non-radioactive benzoic acid on the decarboxylation of [*carboxy*-$^{14}$C]salicylic in aqueous aerated solutions irradiated with $^{60}$Co γ-rays. Dose : $1{\cdot}2\times10^{5}$ rad, pH 9.
× Initial concentration of sodium salicylate, $2{\cdot}9\times10^{-4}$M ;
○ initial concentration of sodium salicylate, $5{\cdot}8\times10^{-4}$M.

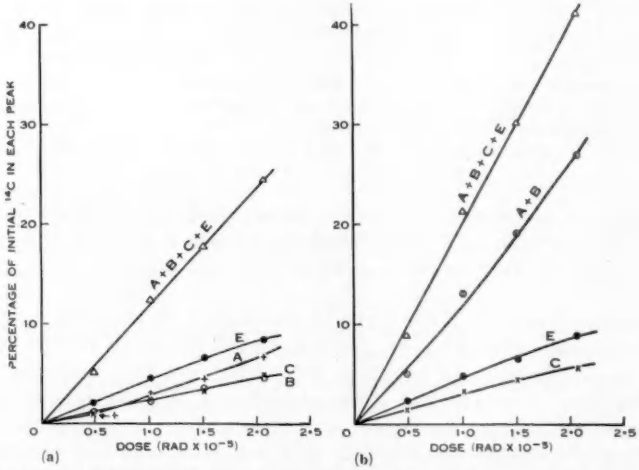


Fig. 5.—Variation with dose of $^{60}$Co γ-rays of scans of chromatograms in solvent 1 of (*a*) [*carboxy*-$^{14}$C]benzoic acid and (*b*) [$^{14}C_7$]benzoic acid. The aqueous aerated solutions of the two types of labelled benzoic acid had the same initial concentrations ($1{\cdot}15\times10^{-3}$M).
*A*, unknown ; *B*, *p*-hydroxybenzoic acid ; *C*, *m*-hydroxybenzoic acid ; *E*, salicylic acid.

by chromatographic "finger printing" (Roberts *et al.* 1955). Bromocresol purple containing formaldehyde (Reid and Lederer 1951) and ferric chloride were used to locate the carrier acids. By the same method 2,5- and 2,3-dihydroxybenzoic acids were identified as products of the irradiation of aqueous [*carboxy*-$^{14}$C]salicylic acid. The 2,4- and 2,6-dihydroxy isomers were not formed.

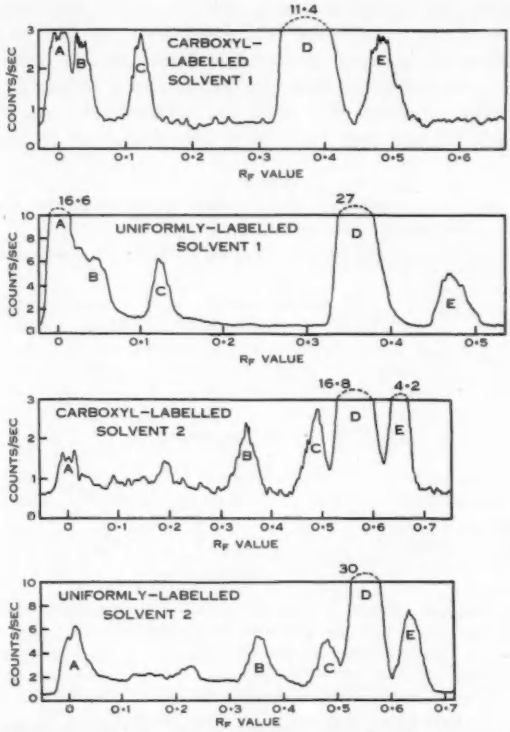


Fig. 6.—Typical scans of chromatograms of irradiated solutions of [$^{14}$C]benzoic acid run in 2 solvent systems. See text for full description.

Some typical results of the scanning of one-dimensional chromatograms are shown in Figures 5 and 6. In this experiment solutions of [*carboxy*-$^{14}$C]benzoic acid (4 ml; $1{\cdot}15\times10^{-3}$M; 0·539 μc/ml) and of [$^{14}C_7$]benzoic acid (4 ml; $1{\cdot}15\times10^{-3}$M; 1·20 μc/ml) were irradiated with $^{60}$Co. The irradiation was interrupted at intervals, and aliquots (0·1 ml) removed and chromatographed in solvent 1. After each sampling the solution was saturated with air before being irradiated again. The chromatograms were scanned and the $^{14}$C content of each peak measured (Fig. 5). Figure 6 shows typical scans of chromatograms run in solvents 1 and 2.

From [*carboxy*-$^{14}$C]benzoic acid the chromatograms in solvent 1 showed the presence of four peaks besides that due to unchanged benzoic acid. Three of these, *E*, *C*, and *B*, in solvents 1 and 2 were identified as *o*-, *m*-, and *p*-hydroxybenzoic acids respectively. The fourth (*A*) with an $R_F$ value of almost zero, was not identified, but was evidently a complex mixture judging by the general spread of radioactivity when this material was run in solvent 2. Peak *A* (solvent 1) presumably contained small amounts of the dihydroxybenzoic acids which have a low $R_F$ value in this solvent (see later). As well as these products there is a considerable amount of decarboxylation as has been shown above. The non-volatile products of the decarboxylation do not appear on the chromatograms of irradiated [*carboxy*-$^{14}$C] acids as radioactive spots. However, the uniformly-labelled benzoic acid loses only one-seventh of its radioactivity on

TABLE 2

ESTIMATION OF MONOHYDROXYBENZOIC ACIDS AFTER IRRADIATION OF AQUEOUS AERATED [$^{14}$C]BENZOIC ACID WITH $^{60}$Co γ-RAYS ($2{\cdot}07 \times 10^5$ RAD)

Results are expressed as percentages of the benzoic acid present initially

| Method of Analysis | [$^{14}C_7$]Benzoic Acid ($1{\cdot}15 \times 10^{-3}$M ; 1·20 μc/ml) | | | [*Carboxy*-$^{14}$C]benzoic Acid ($1{\cdot}15 \times 10^{-3}$M ; 0·539 μc/ml) | | |
|---|---|---|---|---|---|---|
| | *ortho* | *meta* | *para* | *ortho* | *meta* | *para* |
| Estimate from areas of chromatogram "scans" | 8·9 | 5·5 | Not separated | 8·7 | 4·7 | 4·0 |
| Paper chromatography followed by carrier dilution analysis of separated spots | 9·27<br>9·60<br>9·55<br>9·39 } 9·45 | 5·12<br>4·98 } 5·07 | 3·70<br>3·66<br>4·11<br>4·01 } 3·87 | 9·12<br>8·95 } 9·04 | 5·25<br>5·25 } 5·25 | 3·81<br>3·74 } 3·78 |
| Carrier dilution analysis of aliquots irradiated solution without chromatography | 11·3 | 7·3 | 4·8 | | | |

decarboxylation. The differences between the chromatograms of the two types of labelled benzoic acid are therefore due to the carbon atoms of the benzene ring. Figures 5 and 6 show that these decarboxylation products appear in each solvent system in the low $R_F$ region of the chromatograms. Most of this radioactivity is in peak *A* but some of it extends as far as peaks *B* and *C*, contaminating the *p*- and *m*-hydroxybenzoic acids. The monohydroxybenzoic acids were estimated by scanning chromatograms, by carrier dilution analysis of the compounds separated on chromatograms, and by direct carrier dilution analysis of the irradiated solutions. Typical results are given in Table 2. The values obtained for the *m*- and *p*-isomers by direct carrier dilution analysis represent upper limits because the counting rates still had not reached a constant value even after three recrystallizations from water, conversion to the acetyl derivatives, and two recrystallizations of these from aqueous ethanol.

A sample of irradiated aqueous [$^{14}C_7$]benzoic acid (initial concentration $4{\cdot}74\times10^{-3}$ mM 1 μc/mMole; $^{60}$Co; $1{\cdot}14\times10^{6}$ rad) was also examined by carrier dilution analysis for diphenyl. The results showed that diphenyl, if present, could account for a maximum of 2 per cent. of the reaction products after approximately 50 per cent. of the benzoic acid had reacted.

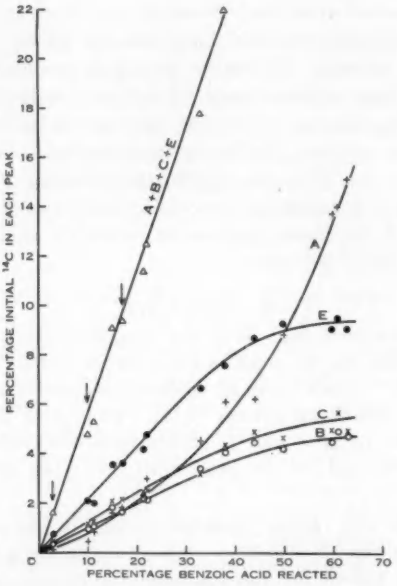


Fig. 7.—Amounts of non-volatile products obtained at various stages in the irradiation of aqueous aerated solutions of [*carboxy*-$^{14}$C]benzoic acid. The amount of $^{14}$C in each peak after chromatography in solvent 1, expressed as a percentage of the $^{14}$C present initially, is plotted against the percentage of benzoic acid which had reacted. The results indicated by arrows were obtained with X-rays (45 kV); the rest were obtained by $^{60}$Co irradiations. *A*, unknown; *B*, *p*-hydroxybenzoic acid; *C*, *m*-hydroxybenzoic acid; *E*, salicylic acid.

During the course of this work numerous aqueous solutions of [*carboxy*-$^{14}$C]benzoic acid with initial concentrations varying from $1{\cdot}8\times10^{-4}$ to $1{\cdot}3\times10^{-2}$M were irradiated with doses of from $3{\cdot}2\times10^{4}$ to $6{\cdot}5\times10^{5}$ rad using either X-rays or $^{60}$Co γ-rays, thus providing solutions in which from 3 to 63 per cent. of the benzoic acid had reacted. In every case chromatography showed that much more salicylic acid was present than either *m*- or *p*-hydroxybenzoic acid which were present in approximately equal amounts. The results of all these irradiations are shown in Figure 7, which shows clearly that the three monohydroxybenzoic acids are primary reaction products from benzoic acid and that they compete with the unchanged benzoic acid for the free radicals present in the water to give compounds which appear as peak *A* in solvent 1.

A similar kinetic study with [*carboxy*-$^{14}$C]salicylic acid and 2nd solvent 3 showed that 2,3- and 2,5-dihydroxybenzoic acids were primary products (initial ratio 2,5 : 2,3 :: 1 : 1·6) which reacted further to form material with low $R_F$ values in the three solvent systems.

Chromatograms of irradiated salicylic acid solution in the alkaline solvents 1 and 2 were misleading. For example, in solvent 1 all the $^{14}$C except that due to salicylic acid remained at or near the origin yet larger amounts of non-radioactive 2,3- or 2,5-dihydroxybenzoic acid had $R_F$ values of 0·20 and 0·24 respectively in this solvent. Evidently the small amounts ($\sim$1 μg) of these labelled compounds were oxidized rapidly in the ammoniacal atmosphere of the chromatography tank, whereas with larger amounts of inactive material only a small percentage was oxidized during chromatography. Chromatograms with various quantities of the 2,3- and 2,5-dihydroxybenzoic acids confirmed this. The oxidation products remained at the origin as a brown stain which appeared to some extent on all the chromatograms in solvents 1 and 2 of the irradiated benzoic and salicylic acid solutions.

## IV. Discussion

The above results show that both the decarboxylation and hydroxylation reactions of benzoic acid may be explained as indirect effects (Bacq and Alexander 1955) of the radiation. Both types of reaction are presumably due to the free radicals formed from the water (Weiss 1944). Thus both the dilution (Figs. 2 and 3) and protection (Figs. 4 and 7) effects were observed. The yields were approximately proportional to the dose until 30–40 per cent. of the benzoic acid had reacted.

The G values for the various products formed in the initial stages of the irradiation of aqueous benzoic acid have been estimated from the results depicted in Figure 7. These values for the monohydroxybenzoic acids were: *ortho*, 0·74; *meta*, 0·42; *para*, 0·33; G($CO_2$) was 0·73. The G value for the total reaction of benzoic acid [G(*benzoic*)] was 2·6. The reason for the discrepancy between G(*benzoic*) and the sum (2·2) of the G values for the products has not been traced.

G($CO_2$) is of the same order as the corresponding values for nicotinic (Goldblith *et al.* 1949) and *o*- and *p*-aminobenzoic acids (Corson *et al.* 1951). The values for these acids are all about 0·58 (calculated from the specific inactivation doses). The G value for the initial stages of the reaction would presumably be closer to the value obtained for benzoic acid. G($CO_2$) for Na salicylate (1·53) is thus exceptionally high.

Of the other values only G(*benzoic*→*salicylic*) can be compared with previously published results. From the data given by Day and Stein (1949), I have calculated G(*benzoic*→*salicylic*) to be 4·53. In the later paper of Loebl, Stein, and Weiss (1951) in which it was stated that Day and Stein's dosimeter was used, a graph was published in which the yield of salicylic acid was plotted against the radiation dose. The G value 0·91, calculated from the graph, is of the same order as the present value.

The chromatographic results show that the *o*-, *m*-, and *p*-hydroxybenzoic acids compete with the remaining benzoic acid for the free radicals. From salicylic acid 2,3- and 2,5-dihydroxybenzoic acid are formed and appear as one spot near the origin of chromatograms run in solvent 1 (peak *A* of Fig. 7) unless previously mixed with carrier. The *meta*- and *para*-isomers probably produce similar dihydroxybenzoic acids and further oxidation products but these isomers were not studied.

The detection of the three monohydroxybenzoic acids by isotope dilution analysis and " radiochromatography " has confirmed the identification of these products by Loebl, Stein, and Weiss (1951). Their results for the *meta*- and *para*-isomers were based on paper chromatography alone, using diazotized *p*-nitroaniline followed by sodium carbonate as the means of detection. However, although the qualitative result has been confirmed the quantitative results are rather different. Every analysis here has indicated that salicylic acid was the major isomer formed, the ratio $o : m : p$ during the early stages of the reaction being about 9 : 5 : 4, whereas the previous authors reported the corresponding ratio to be 5 : 2 : 10 for aerated solutions. These differences do not affect the conclusion that the orientation is indicative of substitution by free radicals. The possibility that the differences were due to the different dose rates, or different radiation energies used cannot be excluded. However, the explanation may be that the estimates by Loebl, Stein, and Weiss were based on the areas of coloured spots only. Their *p*-hydroxybenzoic acid spot might really have been a mixture of compounds which reacted with diazotized *p*-nitroaniline. The results using uniformly $^{14}$C-labelled benzoic acid showed that a lot of the radioactivity that remained near the origin in solvent 1 moved a considerable distance in solvent 2—the solvent used by Loebl, Stein, and Weiss—about as far as *p*-hydroxybenzoic acid. If adequate development was not allowed, these decarboxylation products were not completely separated from the *p*-hydroxybenzoic acid, which then appeared to be the main product. Moreover, separations in solvent 2 were harder to reproduce than in the other solvents. Thus the different results may be explained if it is assumed that the benzoic acid was decarboxylated to the same extent in the experiments of Loebl, Stein, and Weiss as in those reported here and that the non-volatile decarboxylation products gave a colour with diazotized *p*-nitroaniline. Unfortunately, it has not been possible to continue work on the identification of the products of the decarboxylation reaction.

The $o : m : p$ ratio obtained in the present work is very similar to that reported by Boyland and Sims (1953) for the action of hydrogen peroxide ($2 \times 10^{-3}$M) on aqueous benzoic acid under ultraviolet irradiation—$o : m : p :: 10 : 5 : 5$. Bates, Evans, and Uri (1950) investigated the effect of light of wavelength 365 mμ on aqueous solutions of benzoic acid in the presence of the ferric ion pair complex, $Fe^{3+}OH^-$, a system that produces free hydroxyl radicals. Spectroscopic analysis of the reaction mixture showed that all three monohydroxybenzoic acids were formed, $o : m : p$ being 2 : 2 : 1. Here again the *para*-isomer was a minor component.

The further hydroxylation of salicylic acid occurred only in the positions *ortho-* and *para-* to the hydroxyl group already present. This result is analogous to the production of catechol and quinol from aqueous phenol by the action of X-rays (Stein and Weiss 1951), and to the radiolysis of aqueous solutions of tyrosine (Rowbottom 1955) which produced no hydroxylation in the position *meta* to the original hydroxyl group. Similarly Bray, Thorpe, and White (1950) detected only the *o-* and *p*-hydroxylation products in the urine of rabbits after the administration of *o-*, *m-*, and *p*-hydroxybenzoic acids.

More quinol than catechol was always found by Stein and Weiss (1951) in the irradiation of aqueous phenol, the actual ratio depending on the reaction conditions, whereas in the present work more of the *o-* than the *p*-dihydroxybenzoic acid was produced from salicylic acid. However, a preponderance of *ortho*-substitution is by no means new in homolytic reactions. Hey and Williams (1953) reported this effect in the phenylation of some simple benzene derivatives.

Loebl, Stein, and Weiss (1951) reported the formation of diphenyl from the irradiation of aqueous benzoic acid but did not make it clear whether or not the solution was aerated throughout the irradiation. Very little, if any, [$^{14}$C]-diphenyl was formed in the aerated solutions used here. This compares with the results of Baxendale and Smithies (1955), who showed that diphenyl was formed only when aqueous solutions of benzene were irradiated in the absence of air.

In principle, the irradiation of Na [*carboxy*-$^{14}$C]benzoate in aqueous solution followed by carrier dilution analysis for carbonate should provide a more sensitive chemical dosimeter than that of Day and Stein (1949) or the modification described by Carr (1951). Most chemical dosimeters cannot give accurate values for doses less than a few thousand rads. One exception is that of Rudstam and Svedberg (1953), a $^{59}$Fe tracer method which is claimed to measure doses over a range as low as 0–100 rad. If 1 ml samples of dilute aqueous Na [$^{14}$C]benzoate with a specific activity of 1 mc/mMole were irradiated, the disintegration rate of the carbon dioxide produced would be about 1 d/m/rad. Under these conditions a minimum of about 10 rad could be determined using internal gas counters (Christman and Wolf 1955). The sensitivity would increase in proportion to the volume of solution irradiated and to the specific activity of the benzoic acid used, but would decrease if other assay methods were used. Thus the decarboxylation method would be almost as sensitive as the $^{59}$Fe method and the long half-life of $^{14}$C would be an advantage.

It has been assumed throughout this paper that there were no errors due to "isotope effects". This assumption seems justified since the same results were obtained with the carboxy- and uniformly-labelled benzoic acids so far as the hydroxylation products were concerned. In any case, errors from this source, if they do occur, would not be expected to exceed 6 per cent. (Ropp 1952).

## V. Acknowledgments

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# CHEMISTRY OF POLYNUCLEAR COMPOUNDS

## II. THE BEHAVIOUR IN CONCENTRATED SULPHURIC ACID SOLUTION AND ABSORPTION SPECTRA OF SOME POLYNUCLEAR QUINONES

By R. A. Durie* and J. S. Shannon*

[*Manuscript received December 2, 1957*]

*Summary*

In an investigation into the coking mechanism of coal, polynuclear quinones were adopted as models. The electronic absorption spectra of dibenzanthrone (I); 16,17-dimethoxydibenzanthrone (II); 16,17-diethoxydibenzanthrone (III); 16-methoxy-17-ethoxydibenzanthrone (IV); 16-methoxy-17-hydroxydibenzanthrone (V); and 16-ethoxy-17-hydroxydibenzanthrone (VI) in chlorobenzene and dioxane solution were measured and are discussed. Non-planar configurations are proposed for II-VI and the possibility of the same for I considered. The electronic absorption spectra in concentrated sulphuric acid of I, II, V, and VI were measured and are discussed. IV, V, and VI are new vat dyes; V is produced by the action of concentrated sulphuric acid on II and IV, and VI is produced by the same reaction with III. IV is prepared by the methylation of VI. The electronic absorption spectra of anthraquinone and some derivatives were measured in concentrated sulphuric acid and are discussed in conjunction with some of the above spectra. The infra-red spectra of IV, V, and VI confirm the identification of these compounds as 16,17-disubstituted dibenzanthrones and establish the nature of the alkoxyl substituents; the quinonoid-carbonyl frequencies are discussed.

### I. Introduction

As part of a programme aimed at elucidating the chemical reactions involved during the coking of coal, a study is in progress of the pyrolytic reactions and coking of a series of polynuclear quinones. The application of spectroscopic methods in this study began with discussion of the infra-red spectra of these quinones in Part I of this series (Durie, Lack, and Shannon 1957). Since concentrated sulphuric acid has been found to be the best solvent for the pyrolytic residues of most polynuclear quinones, their electronic absorption spectra must be measured in this solvent. Thus any structural studies of these pyrolytic products based on electronic spectroscopic studies require an understanding of the behaviour of the parent quinones in concentrated sulphuric acid.

The present paper discusses the stability and reactions in concentrated sulphuric acid of dibenzanthrone (I); 16,17-dimethoxydibenzanthrone (II); 16,17-diethoxydibenzanthrone (III); and 16-methoxy-17-ethoxydibenzanthrone (IV). The discussion of the results is divided into three parts. In Section II (*a*) the electronic spectra in chlorobenzene and dioxane of I-IV and of 16-methoxy-17-hydroxydibenzanthrone (V) and 16-ethoxy-17-hydroxydibenzanthrone (VI) are discussed in relation to their structure and configuration. Section II (*b*)

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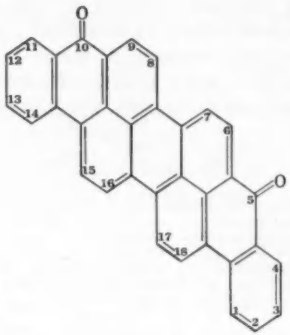
deals with the reactions and electronic spectra in concentrated sulphuric acid of I-VI and some anthraquinone derivatives. The structures of IV, V, and VI have been assigned on the basis of chemical and electronic spectroscopic evidence and confirmed by a study of their infra-red spectra, which are considered in Section II (*c*).



(I)

## II. Results and Discussion

### (*a*) *Electronic Absorption Spectra in Chlorobenzene and Dioxane Solution*

The absorption peaks in the electronic spectra of I-VI in chlorobenzene and dioxane solution are summarized in Table 1, together with available published results. The electronic spectra of I-VI in chlorobenzene solution are presented in Figure 1.

Padhye, Rao, and Venkataraman (1953) measured the electronic spectra of I and II in *o*-chlorophenol solution. The curves presented by these authors are similar in form to those produced in the present work except that they are displaced towards the red, with a small increase in intensity in the curves for the chlorobenzene and dioxane solutions. These bathochromic and hyperchromic effects are no doubt due to greater solute-solvent association in the *o*-chlorophenol than in the chlorobenzene and dioxane solutions.

More recent tabulated data on the electronic spectra of I and II in both ethanol and chlorobenzene solution (Moran and Stonehill 1957) differ considerably with respect to peak positions and intensities from both the present results and those of Padhye, Rao, and Venkataraman. It is possible that Moran and Stonehill failed to obtain complete solution, because of the extremely low solubility of I and II in both ethanol and chlorobenzene. In the present studies it was noticed that although the compounds appeared to dissolve completely in hot dioxane, a very fine crystalline precipitate quickly formed which was very difficult to detect. Consequently, for dioxane solutions only the intensities of the comparatively soluble diethoxy compound III are presented in Table 1.

Padhye, Rao, and Venkataraman (1953) have shown by means of a scaled drawing and by the construction of a molecular model that the existence of

normal bond angles and lengths in II would result in considerable overcrowding of the vicinal methoxyl groups.

The effects of overcrowding in condensed aromatic molecules have been subject to increased attention recently. Friedel (1957) has reviewed the electronic spectra of some overcrowded aromatic compounds. He has attributed the bathochromic shifts and intensity changes in the spectra of 4,5-dimethylphenanthrene (VII) and 4,5-dimethylchrysene (VIII), compared with the spectra of their respective parent hydrocarbons, to strain in the bonds of the entire aromatic nucleus (ring strain) rather than to disruption of coplanarity of the hindered substituents, although he accepts X-ray evidence (Harnik, Herbstein,

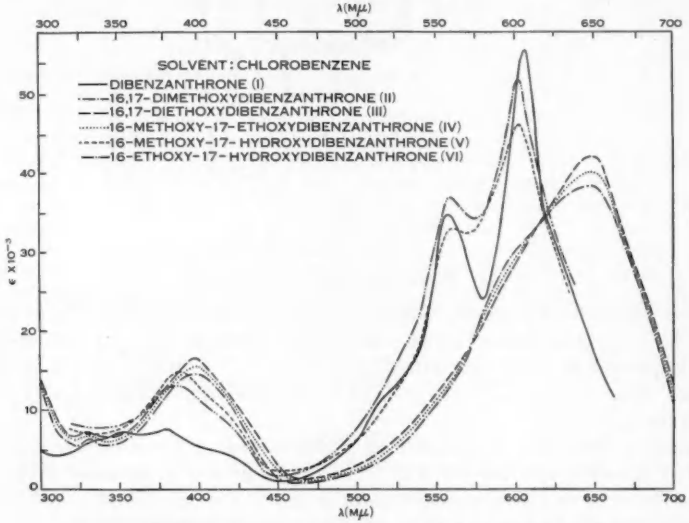



Fig. 1.—Electronic spectra of structures I-VI in chlorobenzene.

and Schmidt 1951) which has shown that ring strain in 3,4-benzphenanthrene (IX) is sufficiently large to cause the aromatic nucleus of IX to become non-planar. X-ray results have also revealed that the molecules X, XI, and XII are distorted (Speakman 1956). Hexahelicene (XIV) (Newman 1956) and 1,12-dimethylbenzo-(c)-phenanthr-5-yl acetic acid (XIII) (Newman and Wise 1956) have been optically resolved, proving these compounds are non-planar. The latter authors from a consideration of X-ray results (Harnik *et al.* 1954 ; Harnik and Schmidt 1954) have concluded that asymmetry within a molecule such as XIII is produced by distortion of the aromatic rings and by non-coplanar methyl groups, but the extent to which the exocyclic groups may be bent before the aromatic nucleus becomes non-planar is not known, ultraviolet spectra failing to distinguish between the two effects.

Padhye, Rao, and Venkataraman (1953) suggested that in II a readjustment of bond angles and lengths occurs to allow the methoxyl groups to remain

coplanar with and to conjugate with the polycyclic system. They attributed the bathochromic and hypochromic shift of the maximum absorption peak in the electronic spectrum of II compared with the corresponding peak in the spectrum of I to this effect. These authors considered that the expected large resonance

TABLE 1

ABSORPTION PEAKS IN ELECTRONIC SPECTRA OF SOME POLYNUCLEAR QUINONES

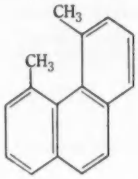
| Quinone | Solvent | | | |
|---|---|---|---|---|
| | Dioxane* | Chlorobenzene* | Chlorobenzene† | *o*-Chlorophenol‡ |
| Dibenzanthrone (I) .. | 259 (—)§<br>552 (—)<br>597 (—) | 380 (7700)<br>558 (34,800)<br>606–8 (55,700) | 404 (10,500)<br>423 (14,100)<br>443 (14,800)<br>507 (1520)<br>564 (1860) | 355 (15,540)<br>365 (15,540)<br>594 (44,810)<br>642 (63,810) |
| 16 , 17 - Dimethoxydibenzanthrone (II) | 262 (—)<br>328 (—)<br>394 (—)<br>634 (—) | 398 (14,600)<br>648–52 (38,600) | 465 (11,200)<br>613 (14,100)<br>655 (12,900) | 400 (15,380)<br>685 (37,000) |
| 16 , 17 - Diethoxydibenzanthrone (III) | 262 (45,000)<br>328 (3700)<br>394 (13,800)<br>634 (32,000) | 398 (16,500)<br>650 (42,200) | | |
| 16 - Methoxy - 17 - ethoxy - dibenzanthrone (IV) | 262 (—)<br>328 (—)<br>394 (—)<br>634 (—) | 398 (15,600)<br>650 (40,000) | | |
| 16 - Methoxy - 17 - hydroxy - dibenzanthrone (V) | 333 (—)<br>385 (—)<br>558 (—)<br>599 (—) | 388 (13,200)<br>560 (33,000)<br>603 (48,000) | | |
| 16 - Ethoxy - 17 - hydroxy - dibenzanthrone (VI) | 333 (—)<br>385 (—)<br>558 (—)<br>599 (—) | 388–9 (15,000)<br>560 (36,800)<br>602–5 (51,800) | | |

* Present work. † Moran and Stonehill (1957). ‡ Padhye, Rao, and Venkataraman (1953). § $\lambda_{max.}$ (mμ), ($\varepsilon_{max.}$)

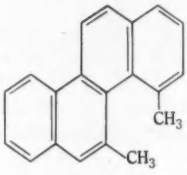
energy of II would prohibit any tendency of its polynuclear aromatic system to exist in a non-planar configuration. This argument seems to be invalidated by the proved non-planarity of molecules such as XII.

The spectrum of II is probably best explained by assuming a buckling of its aromatic nucleus. An examination of the 36 Kekulé forms of II reveals that all contain two single carbon-carbon bonds in the positions illustrated in the formula of II. It would therefore seem that in the resonance hybrid these

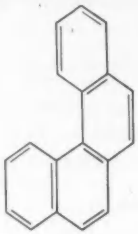
two carbon-carbon bonds would have fairly strong single-bond character and the contribution made by the 36 Kekulé forms to the resonance energy of II should not be significantly affected by a twisting of the molecule about an axis




(VII)

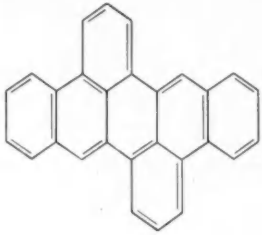



(VIII)

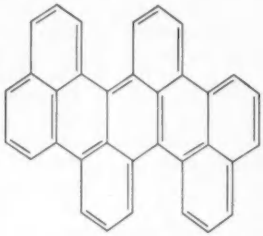


(IX)

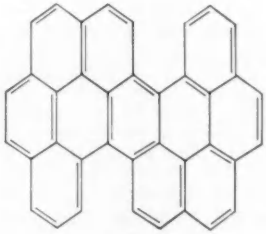
"ab" (as illustrated) linking the two benzanthrone moieties. On the other hand, considerable resonance across these "single" carbon-carbon bonds is indicated by the large red shifts in the spectrum of II compared with the spectrum of 4,4′-dibenzanthronyl, which has its maximum peak at $\lambda_{max.}$ 411 mμ, $\varepsilon_{max.}$



(X)



(XI)

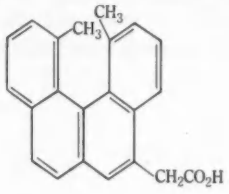


(XII)

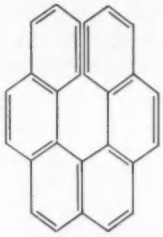
69,500 (Padhye, Rao, and Venkataraman 1953). In this regard it is known that non-coplanarity of two linked aromatic residues does not necessarily eliminate resonance between them, for example, the electronic spectra of *oo′*-dimethoxydiphenyl and 9,10-dihydrophenanthrene both show diphenyl type

absorption related to uninterrupted resonance between the two phenyl groups, as well as contributions from their respectively separated non-coplanar phenyl chromophores (Beaven *et al.* 1952).

In II, resonance across the carbon-carbon bonds linking the methoxybenzanthrone moieties may be contributed to by the types of canonical forms indicated by (*a*) and (*b*) below. The stability of (*b*), due to the presence of

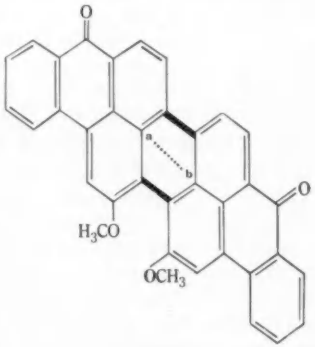



(XIII)



(XIV)

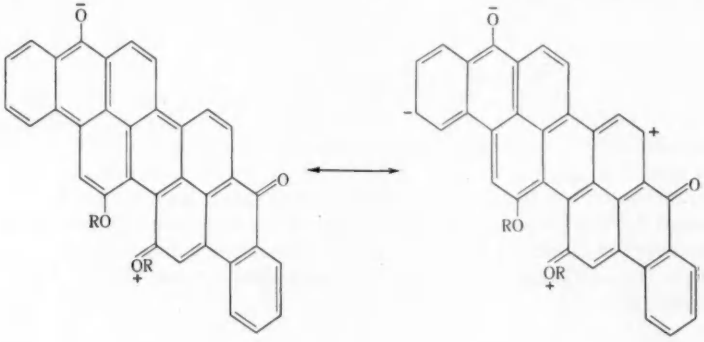
single carbon-carbon bonds in the positions illustrated, may not be significantly decreased by the proposed twisting of the aromatic system. A comparison of the carbonyl frequency of II with I and/or benzanthrone does indicate resonance between the methoxyl groups and the polycyclic system (Durie, Lack, and Shannon 1957).




(II)

Because of the possibility of resonance of the type depicted by forms (*a*) and (*b*), it is not clear to what extent (if any) characteristic absorption of the separated methoxybenzanthrone chromophores will contribute to the electronic absorption of II. Inspection of the present absorption data (Fig. 1 and Table 1) discloses that in addition to the large shift of its maximum-wavelength absorption peak relative to the spectrum of I, the spectrum of II in chlorobenzene solution does not contain the intense dibenzanthrone (I) peak at 558 mμ but does have a fairly strong band at 398 mμ compared with only a very weak band at 380 mμ

in I. These data may indicate that the strong band at 558 mμ in I is related to uninterrupted conjugation throughout the polycyclic system, and the medium band at 398 mμ in II to the absorption of the isolated methoxybenzanthrone moieties. No absorption data for 5-methoxybenzanthrone appear to be available, but in ethanol solution benzanthrone has $\lambda_{max.}$ 394 mμ, $\varepsilon_{max.}$ 10,000; and 4,4′-dibenzanthronyl $\lambda_{max.}$ 411 mμ, $\varepsilon_{max.}$ 69,500 (Padhye, Rao, and Venkataraman 1953). Although it is realized that absorption at 398 mμ in II could conceivably arise from the auxochromic effect of the methoxyl groups it is perhaps noteworthy that according to the data of Padhye, Rao, and Venkataraman the uncrowded 3,12-dimethoxydibenzanthrone does not significantly absorb in this region.

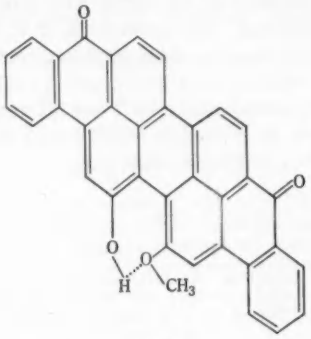



(a) (b)

The replacement in II of one methyl group with a hydrogen atom, to yield V, eliminates the large bathochromic and, to a major extent, the hypochromic shift of the absorption peak of maximum wavelength in II with respect to I; also the peak in I near 558 mμ reappears in V as a high shoulder at 560 mμ. This may indicate that the structural change has eliminated much of the molecular strain and/or non-planarity, since the latter spectral changes would not be predicted on electronic grounds as the order of magnitude of the electronic effects of a hydroxyl and a methoxyl group are roughly similar. The decrease in steric hindrance in V is probably not solely due to the replacement of a comparatively bulky methyl group by a hydrogen atom, but also to the reduction in repulsive forces between the hydroxyl and methoxyl groups due to strong hydrogen bonding (cf. Coulson 1957). The band in the spectrum of II at 398 mμ which has been tentatively associated with a benzanthrone-type absorbing species appears in V at 388 mμ. If the assignment of this band is correct, the evidence would suggest that V is non-planar but the molecular strain is less than it is in II.

Also of interest in relation to the electronic absorption of V is that in dioxane solution its maximum-wavelength absorption peak is shifted 2 mμ towards the red and in chlorobenzene solution 3–5 mμ towards the blue, with respect to the corresponding peak in I. This suggests that solute-solvent association effects

between I and chlorobenzene are more powerful than between V and chlorobenzene and in the former case the resulting bathochromic effect is greater than the combined auxochromic effects of the substituted hydroxyl and methoxyl groups in V. Whether or not V is planar there is evidence that the hydroxyl and methoxyl substituents are in conjugation with the polycyclic system and this is discussed in Section II (*c*) of this paper.




(V)

The electronic absorption spectra of III and IV differ from II only in respect of small changes in intensity, which may be due to the slightly greater steric and electronic influences associated with the ethoxyl group over and above those of the methoxyl group. However, the overall similarity of these spectra suggests that arguments propounded in regard to the configuration of II hold for III and IV. Likewise, conclusions regarding the spectrum and configuration of V are considered to hold for VI.

In conclusion, it is realized that unequivocal X-ray evidence and/or the resolution of optical isomers is needed to elucidate positively the configuration of II-VI. In view of the non-planarity of the hydrocarbons IX-XII, in which any overcrowding is at most due to overlapping of hydrogen atoms, the possibility of dibenzanthrone (I) being slightly distorted owing to overlapping of the hydrogen atoms in the 16,17-positions, cannot at this stage be rejected, although the degree of buckling would of necessity be less than in the 16,17-disubstituted derivatives (II-VI).

### (*b*) *Reactions in Concentrated Sulphuric Acid*

The stability of I and its dialkoxyl derivatives in concentrated sulphuric acid was found to decrease in the order I > II > IV > III. I is very stable and may be recovered unchanged even after the acid solution has been heated to 90 °C; in fact this is an accepted method for purification of I. No variation with time was observed in the electronic spectrum of I in acid solution. However, the spectra of II, III, and IV begin to alter immediately these three compounds are dissolved in sulphuric acid. The relative rates of change were found to be 1 : 200 : 50 respectively. It was not possible to record the true spectra of III and IV in concentrated sulphuric acid; the spectra obtained were represented

by curves intermediate between those reported for II and the products VI and V of the acid hydrolysis of III and IV respectively.

The compounds IV, V, and VI are new dyes which may be recrystallized from nitrobenzene ; IV and V dye cloth green, and VI dyes it blue. V is isolated by precipitation with water after the reaction of II and IV with concentrated sulphuric acid ; VI is similarly produced from III ; and IV is obtained by methylation of the sodium salt of VI. The structure of IV follows from its electronic and infra-red spectra. The structures of V and VI were established by virtue of their infra-red spectra, their analyses, and their capacity to form monosodium salts which when treated with dimethyl sulphate yielded II and IV respectively. The Zeisel determinations on V and VI were usually 20–30 per cent. low ; this observation may be related to resistance of the monoalkoxyl group to hydrolysis by concentrated sulphuric acid.

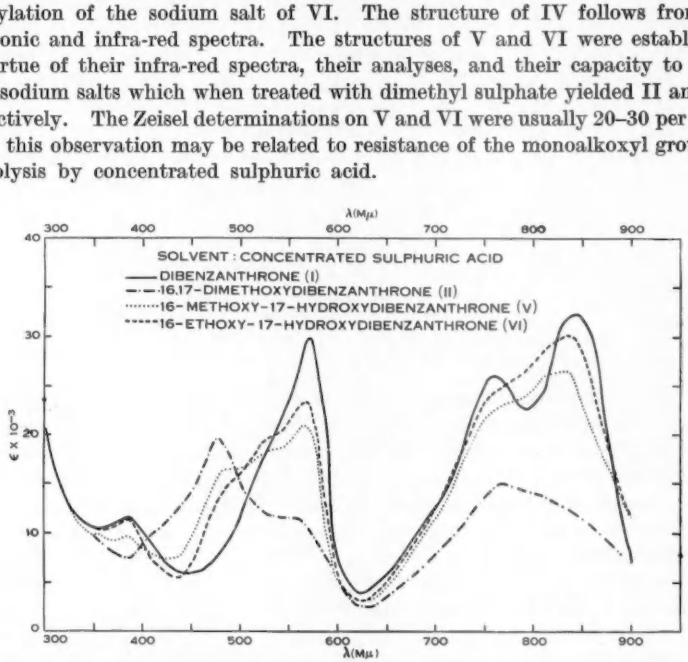



Fig. 2.—Electronic spectra of structures I, II, V, and VI in concentrated sulphuric acid.

The electronic spectra of I, II, V, and VI in concentrated sulphuric acid are presented in Figure 2.

It is well established that polynuclear quinones in the Lewis sense are basic and dissolve in concentrated sulphuric acid ; in fact, the latter has become the most widely used solvent for anthraquinone derivatives, which are so widely used in the vat dye industry (Coffey 1953). There is not, however, very much published literature relating to the structures of the species produced by the solution of quinones in concentrated sulphuric acid.

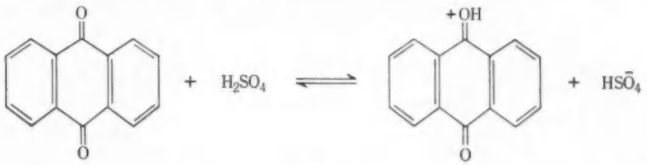
Thomson (1936) reported that II dissolved in concentrated sulphuric acid to form a cherry-red solution which changed to green on the addition of an oxidizing agent. The same author showed that the green solution was still associated with the molecule, II, and no dealkylation occurred until the sulphuric-

nitric acid solution of II was added to excess water, when 16,17-diketodibenzanthrone was produced.

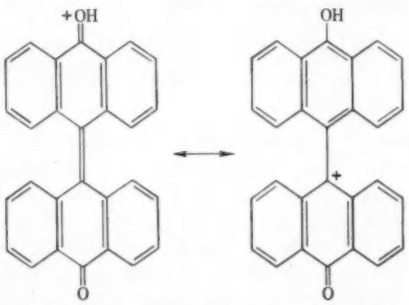
Geake (1941) attributed the solution of anthraquinonoid vat dyes in concentrated sulphuric acid to the formation of resonance-stabilized " quinonium " ions, for example,

and showed that some of these ionic species are capable of reversible oxidation and/or reduction.

Hammett and Deyrup (1933) have demonstrated by means of cryoscopic measurements that with anthraquinone only one of its carbonyl oxygen atoms is protonated in concentrated sulphuric acid :



Hebert, Goren, and Vernon (1952) have measured the absorption spectra of $\Delta^{10,10'}$-bianthrone, helianthrone, and *meso*naphthobianthrone in concentrated sulphuric acid solution and suggest that protonation of one or both of the carbonyl oxygen atoms could have occurred. They suggest that protonation permits the formation of resonance hybrids which have contributing charged structures analogous to the well-known halochromic salts, e.g. with $\Delta^{10,10'}$-bianthrone :



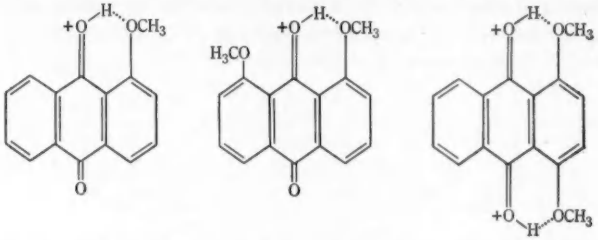
These authors also reported that cryoscopic measurements for these quinones in sulphuric acid were not interpretable.

Handa (1955) has measured $pK_B$ values of some polynuclear quinones in concentrated sulphuric acid solution and has also suggested that protonation occurs on their carbonyl oxygen atoms.

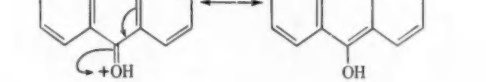
In the absence of accurate cryoscopic measurements it is not possible to state positively whether one or both carbonyl oxygen atoms of I are protonated by sulphuric acid, but there would be a greater chance of resonance stabilization

of the diprotonated form of I than that of the mono-acid base, anthraquinone. In one of the theories advanced (below) to explain the large hypsochromic shift in the spectrum in concentrated sulphuric acid of II relative to I it has been assumed that protonation of both the carbonyl oxygen atoms in I does occur.

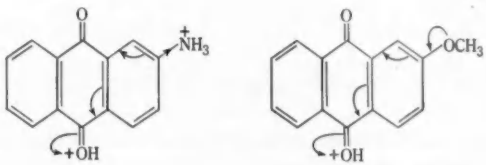
Since acid hydrolysis of alkoxyl groups is initiated by protonation of alkoxyl oxygen atoms (Ghaswalla and Donnan 1936; Remick 1950) it is apparent that one or both alkoxyl groups in II, III, and IV are protonated in concentrated sulphuric acid. However, it is not usual for alkoxyl groups to be protonated by concentrated sulphuric acid if they are attached to molecules containing other electron-attracting basic centres (cf. Wiles 1956), e.g. Wiles and Baughan (1953)



found that methoxyl-group protonation occurred when *p*-methoxyacetophenone and *p*-methoxybenzoic acid dissolved in sulphuric acid but did not occur in methoxyanthraquinones although α-methoxyl groups stabilize, by hydrogen bonding, the protonation of the quinone groups. Thus 1,4-dimethoxyanthraquinone is a diacid base whereas anthraquinone, 1-methoxyanthraquinone, and



(1) (2)



(3) (4)

1,8-dimethoxyanthraquinone are mono-acid bases. Since the methoxyl groups of methoxyanthraquinones do not protonate they should exert their normal auxochromic effect on the electronic spectra of their parent compounds in concentrated sulphuric acid solutions. This has been confirmed by the large bathochromic shifts shown in the spectra of 1,4-, 1,5-, and 1,8-dimethoxy-

anthraquinone with respect to anthraquinone (Table 2). On the other hand, the absorption peaks of maximum wavelength of 1-amino-, 2-amino-, and 1,2-diaminoanthraquinone in concentrated sulphuric acid solution are shifted to shorter wavelengths and lower intensities compared with anthraquinone (Table 2). These latter effects are most probably caused by the protonation of the basic amino group.

If forms (1) and (2) are the main contributing resonance structures of anthraquinone dissolved in concentrated sulphuric acid (cf. Durie, Lack, and Shannon 1957) then the introduction of a strongly electron-attracting cationic centre, for example $-\overset{+}{N}H_3$ (form (3)), will inhibit the mesomeric shifts leading to structures such as (2) and a hypsochromic shift will result. The introduction of an electron-donating group, for example, OMe, will facilitate the depicted mesomeric shift, for example, form (4), and a bathochromic shift in the visible spectrum will occur (cf. Peters and Sumner 1953).

TABLE 2

ELECTRONIC ABSORPTION PEAKS OF ANTHRAQUINONE AND SOME DERIVATIVES IN CONCENTRATED SULPHURIC ACID SOLUTION

| | | | | | |
|---|---|---|---|---|---|
| Anthraquinone | 270 (149,000)* | 313 (9400) | 410 (7400) | | |
| 1-Aminoanthraquinone | 264 (32,300) | 380 (3800) | | | |
| 2-Aminoanthraquinone | 262 (62,000) | 375 (7100) | | | |
| 1,2-Diaminoanthraquinone | 262 (52,700) | 360 (6600) | | | |
| 1,4-Dimethoxyanthraquinone | 252 (109,000) | 277 (155,000) | 335 (27,700) | 530 (80,400) | 572 (113,000) |
| 1,5-Dimethoxyanthraquinone | 265 (209,000) | 332 (30,600) | 538 (87,000) | 580 (118,000) | |
| 1,8-Dimethoxyanthraquinone | 304 (14,000) | 339 (5720) | 528–32 (25,800) | 615 (10,200) | |

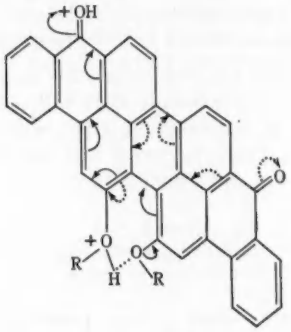
* $\lambda_{max.}$ (mμ), ($\varepsilon_{max.}$).

Alkoxyl group protonation may cause the large hypsochromic shifts in the spectra of concentrated sulphuric acid solutions of II, compared with I. Two explanations of the alkoxyl group protonation in II, III, and IV which occurs despite the presence of the basic quinone groups, may be considered.

(i) Conjugation between the alkoxyl groups and the respective polycyclic systems is depressed to some extent by bond strain, which still persists despite the proposed twisting of the polycyclic systems; or

(ii) protonation of one alkoxyl group, stabilized by hydrogen bonding to the second alkoxyl group. Thus II in concentrated sulphuric acid solution would contain one electron-attracting and one electron-donating substituent. It would follow then that, other things being equal, any net effect of these substituents on the spectrum of II relative to I would be small for reasons discussed above. However, this is not in accord with the large blue shifts in the spectrum of II relative to I illustrated in Figure 2, and therefore it is possible that the electronic absorption of I in sulphuric acid is associated with protonation

of both quinone groups, whereas in II, III, and IV the stabilized cationic centre on one alkoxyl group depresses the basicity of one of the quinone groups and prevents its protonation. On the other hand, the unprotonated alkoxyl group, by virtue of its $+T$-effect, could activate the other quinone group and facilitate its protonation. These two electronic effects are illustrated below in the proposed formula of the absorbing species :

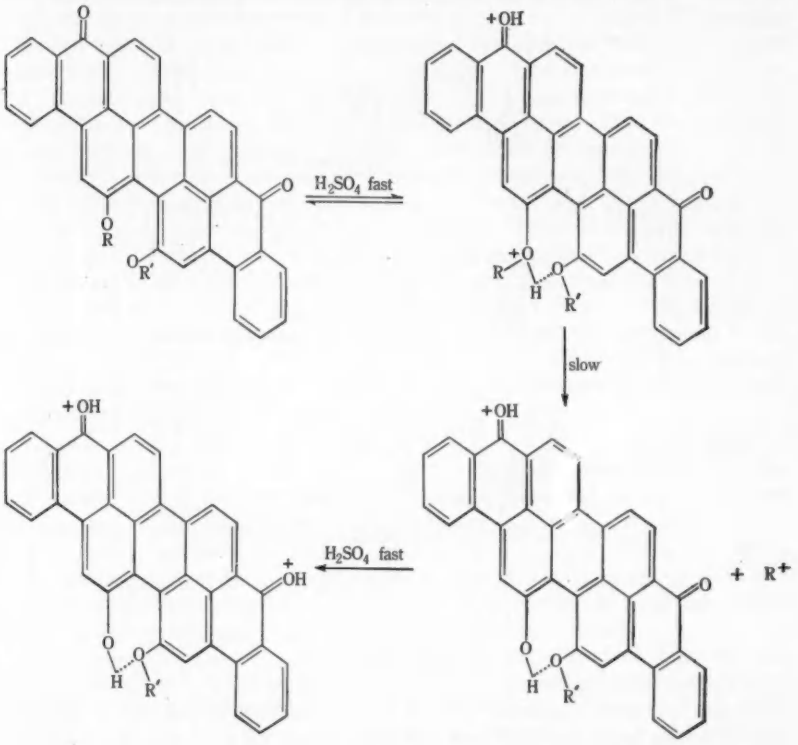



The second explanation is favoured since (*a*) no dihydroxydibenzanthrone has been detected from the reaction with concentrated sulphuric acid of II, III, and IV ; and (*b*) there would be less steric strain with monoprotonation and hydrogen bonding than with diprotonation. With IV, which contains both a methoxyl and an ethoxyl group and which yields only V after reaction with concentrated sulphuric acid, it would follow that protonation occurs on the ethoxyl oxygen atom. This is in accord with the slightly greater basicity of the ethoxyl group expected by virtue of the slightly greater $+I$-effect of the ethyl compared with the methyl residue.

If it is now assumed that the hydrolysis is of the $S_N$ 1 type (cf. Remick 1950) and the bond broken is the *O*-alkyl, then the reaction may be depicted as shown on the opposite page.

The factors that would influence the slow rate-controlling step are (i) the resonance stabilization of $R^+$ and (ii) the ionic strength of the O—R bond that is broken. In the hydrolysis of III and IV, $R^+$ in each case is $C_2H_5^+$, so that (ii) must be the factor responsible for the faster hydrolysis of III. The ionic bond strength would be decreased both by the presence of electron-releasing groups and by steric hindrance capable of producing bond strain. For example, saturated cyclic ethers are more susceptible to hydrolysis than simple aliphatic ethers, the ease of hydrolysis increasing as the ring becomes smaller and therefore the strain larger (Remick 1950). It is known that there must be considerable strain associated with the alkoxyl groups in III and IV and it is well established that hindrance with ethyl groups is greater than with methyl groups. Therefore in terms of steric hindrance prediction of the rates of hydrolysis is in accord with observation. Also the greater $+T$-effect of the unprotonated ethoxyl group in III compared with the corresponding effect of the unprotonated methoxyl

group in IV, would produce a greater net flow of electrons towards the O—R bond to be broken in III than in IV. Hence the prediction of relative rates based on comparative electronic influences agrees with observation and the overall effect may therefore be produced by a combination of both the steric and the electronic influences. The even slower hydrolysis of II compared with III and IV may be attributable not only to a smaller combined contribution of these previous effects but also to the smaller resonance stabilization of $CH_3^+$ compared with $C_2H_5^+$ which is produced in the hydrolysis of both III and IV.




There are only small differences between the spectra of V and VI in concentrated sulphuric acid. These closely resemble the spectra of I in the same solvent, but the absorption peaks at maximum wavelength in the spectra of V and VI are shifted slightly towards the blue with respect to the corresponding peak in I. It would appear that solvation effects between I and concentrated sulphuric acid have a greater bathochromic effect than do the substituents in V and VI and the presence of these substituents inhibits the degree of solvation in V and VI. These are analogous effects to those encountered in chlorobenzene solution.

The resistance to hydrolysis of the monoalkoxyl groups in V and VI may be related to the strong hydrogen bonding between the hydroxyl and alkoxyl groups persisting in the concentrated sulphuric acid solution, thus inhibiting protonation of the monoalkoxyl groups. Further the decreased overcrowding in V and VI compared with that in II, III, and IV would facilitate the operation of the $+T$-effect of the monoalkoxyl groups, thereby decreasing their basicity and consequently their ability to accept a proton.

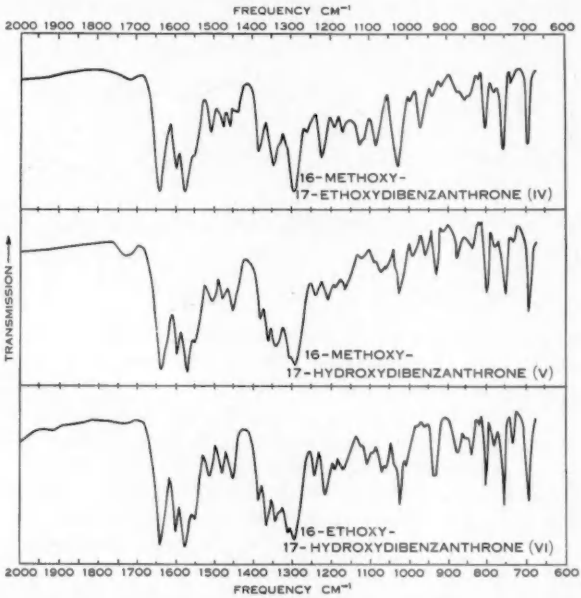



Fig. 3.—Infra-red spectra between 2000 and 650 $cm^{-1}$ of structures IV, V, and VI.

### (c) *Infra-Red Spectra*

The infra-red spectra between 2000 and 650 $cm^{-1}$ of IV, V, and VI are presented in Figure 3. The spectra of I, II, and III appeared in Part I of this series (Durie, Lack, and Shannon 1957).

There is a marked similarity in the overall spectra of all these molecules. The greatest differences occur in the "fingerprint" region between 1200 and 900 $cm^{-1}$ which serves to identify positively each species. There are significant similarities and differences elsewhere in the spectra of these molecules which provide useful information on their structure. These are discussed in detail below.

(i) *Evidence for Presence of —OH Substituents.*—As stated earlier, both V and VI form monosodium salts which react with dimethyl sulphate to form *O*-methyl compounds. This behaviour indicates the presence in V and VI of

a hydroxyl group either as a simple substituent or hidden in a keto-enol system. The absence of any carbonyl absorption, apart from the quinonoid carbonyl band in the infra-red spectra of these compounds, indicates that no keto form is present unless this is absorbing at the same frequency as the quinonoid carbonyl groups, which is unlikely. Thus a hydroxyl group substituent is indicated. Since no discrete absorption which can be attributed to the hydroxyl-stretching vibration occurs in the infra-red spectra of V and VI the hydroxyl group must be participating in strong intramolecular hydrogen bonding. Nakamoto, Margoshes, and Rundle (1955) state that in general, as the strength of hydrogen bonding in a system increases, the absorption in the infra-red due to the hydroxyl-stretching vibration shifts towards lower frequencies and becomes less prominent. Flett (1948) was unable to detect any hydroxyl-stretching vibration band in the mono- and disubstituted hydroxyanthraquinones where intramolecular hydrogen bonding between the hydroxyl group, or groups, and one or both of the quinonoid carbonyl groups, was possible. However, Hadzi and Sheppard (1954) studied the effect of deuteration on the spectra of these molecules and showed that there is overlapping absorption due to both the hydroxyl and CH groups in the 3000 $cm^{-1}$ region. On the other hand, Josien *et al.* (1953) were unable to locate any hydroxyl absorption for 5,8-dihydroxynaphthaquinone, 1-hydroxyphenanthraquinone, or dihydroxynaphthacenequinone, and state that there is no overlapping absorption in the C—H stretching-vibration region. The results of the present work also indicate that overlapping OH and CH absorption in the 3000 $cm^{-1}$ region of the spectra of V and VI is unlikely, since only weak discrete absorption occurs in this region and this can be assigned confidently to the C—H stretching-vibrations of the alkoxyl substituents (see below).

Josien *et al.* (1953) have postulated that the —OH absorption loses its identity only when this group can form with a carbonyl group a six-membered ring system which becomes resonance-stabilized, resulting in a symmetrical —O . . . H . . . O group. The results of Hadzi and Sheppard (1954) do not support this hypothesis. In V and VI hydrogen bonding of the OH group with the alkoxyl substituent would result in a seven-membered ring system and resonance stabilization would be unlikely, since the weight of available experimental evidence suggests that these molecules are non-planar.

The spectra of the 16,17-dialkoxy-substituted dibenzanthrones II, III, and IV, and of the 16-alkoxy, 17-hydroxydibenzanthrones V and VI, show a close similarity in the region 1300–1400 $cm^{-1}$, the spectra of the latter differing from those of the former only by the presence of two additional bands near 1365 and 1310 $cm^{-1}$. These bands may be associated with the OH group but deuteration studies would be necessary to establish this correlation. Hadzi and Sheppard (1954) in their deuteration studies on hydroxyanthraquinones were able to associate absorption peaks near 1300 $cm^{-1}$ with the OH groups present and assigned them to coupled C—O stretching and O—H in-plane deformation vibrations. These peaks are more pronounced than the overlapping OH and C—H stretching-vibration bands in the hydroxyanthraquinones.

(ii) *Characterization of the Alkoxyl Substituents.*—A comparison of the spectra in the region 2800–3100 $cm^{-1}$ of compounds II to VI as well as those of

5,10,16,17-tetramethoxy- ; 5,10,16-trimethoxy-17-ethoxy- ; 5,10-dimethoxy-16,17-diethoxy- ; and 5,10-dimethoxyviolanthrenes* (Fig. 4 and Table 3) reveals a correlation which is of use in the characterization of alkoxyl substituents in this class of compound. An absorption peak near 2840 $cm^{-1}$ as well as a stronger peak near 2940 $cm^{-1}$ always accompany the presence of methoxyl substituents. The presence of an ethoxyl substituent is always associated with a peak near 2990 $cm^{-1}$ and a weaker peak near 2930 $cm^{-1}$. The peak near 2840 $cm^{-1}$ does not occur when only ethoxyl substituents are present, but a weak shoulder may appear near 2990 $cm^{-1}$ when only methoxyl groups are present if the 2840 $cm^{-1}$ methoxyl absorption is strong. However, this does not affect the usefulness of a distinct 2990 $cm^{-1}$ band for the diagnosis of ethoxyl groups in the class of

TABLE 3

C–H STRETCHING FREQUENCIES IN ALKOXY-SUBSTITUTED DIBENZANTHRONES AND VIOLANTHRENES

| Alkoxy Substituted | Substituents | C–H Frequencies ($cm^{-1}$) | | | | |
|---|---|---|---|---|---|---|
| | | Aromatic CH | $C_2H_5O$ | | | $CH_3O$ |
| (1) 16,17-Disubstituted dibenzanthrones | Dimethoxy (VII) .. | 3065 | | 2940 | | 2840 |
| | Diethoxy (III) .. | 3070 | 2985 | 2930 | 2885 | |
| | Methoxyethoxy (IV) | 3070 | 2985 | 2940 | | 2840 |
| | Hydroxyethoxy (V) | 3070 | | 2940 | | 2845 |
| | Methoxy (VI) | 3070 | 2985 | 2930 | | |
| (2) Substituted violanthrenes | 5,10,16,17-Tetramethoxy | 3070 | (3000) | 2940 | | 2840 |
| | 5,10,16-Trimethoxy-17-ethoxy | 3080 | 2990 | 2940 | | 2845 |
| | 5,10-Dimethoxy-16,17-diethoxy | 3085 | 2990 | 2940 | | 2840 |
| | 5,10-Dimethoxy .. | 3060 | | 2940 | | 2845 |

compound under study ; for example, the distinct 2990 $cm^{-1}$ ethoxyl band in the spectrum of trimethoxymonoethoxyviolanthrene should be noted (Fig. 4 (*b*)). The presence of a pronounced band near 2850 $cm^{-1}$ in the spectra of 1,4- ; 1,5- ; and 1,8-dimethoxyanthraquinone serves to confirm the correlation of a band near this position in the spectrum of a compound with the presence of methoxyl groups. However, a distinct band near 2990 $cm^{-1}$ in the spectra of 1,4- and 1,5-dimethoxyanthraquinone shows that, in general, a band near this position in the spectrum of a compound must be used with caution to predict ethoxyl groups (Durie and Shannon, unpublished data).

Thus it is evident from the C—H stretching-vibration region of the infra-red spectra that the hydrolytic products of II and III in sulphuric acid still contain methoxyl or ethoxyl groups respectively and that the ethoxyl group is hydrolysed

* Complete spectroscopic (electronic and vibrational) and preparative details for these substituted violanthrenes will be published later.

in preference to the methoxyl group in IV. The identical overall spectra of the products from II and IV in sulphuric acid further confirm the latter conclusion.

Henbest *et al.* (1957) have recently concluded that the symmetrical C—H stretching-vibration in methoxyl groups occurs between 2810 and 2840 $cm^{-1}$

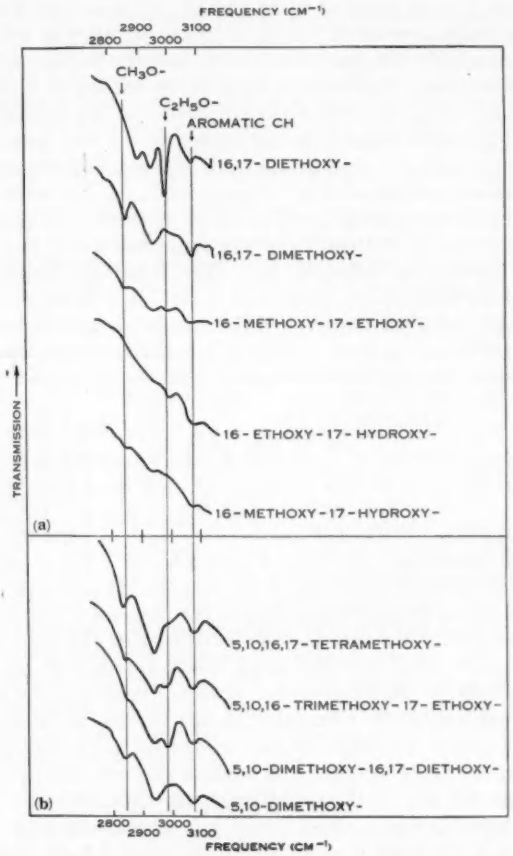



Fig. 4.—C–H stretching-vibrations-characteristic absorption in $CH_3O$ and $C_2H_5O$ groups.

(*a*) 16,17-Disubstituted dibenzanthrones.

(*b*) Alkoxy-substituted violanthrenes.

and that the asymmetrical C—H stretching-vibration of $-CH_3$ groups in both methoxyl and ethoxyl groups occurs between 2970 and 3000 $cm^{-1}$. The present correlations are in agreement with these suggestions, but it is apparent that the intensity of the asymmetrical C—H stretching-vibration of the $-CH_3$ group is

much higher in the ethoxyl than in the methoxyl group for the alkoxy-substituted dibenzanthrones and violanthrenes.

(iii) *Quinonoid Carbonyl Frequencies.*—V and VI have quinonoid carbonyl frequencies at 1640 $cm^{-1}$. A close inspection of composite single-beam scans, made under conditions of maximum resolution, indicates that these frequencies are slightly higher than those of II-IV, which all occur at 1637 $cm^{-1}$.* The carbonyl bands in the spectra of V and VI are of comparable width, as are the corresponding bands in the spectra of I-IV, but the former are significantly broader than the latter. The broader band in the spectra of V and VI may be due to differences in the electron-donating powers of the alkoxy and hydroxy substituents which cause slight non-equivalence of the two quinonoid carbonyl groups in the molecules, for reasons discussed in Part I of this series by Durie, Lack, and Shannon (1957).

The carbonyl frequencies of II, III, and IV relative to that of I show that, despite the non-planarity of these molecules suggested above, there is resonance between their alkoxyl substituents and their respective polycyclic systems. The lowering of the carbonyl frequencies of V and VI with respect to the corresponding frequencies of benzanthrone (1649 $cm^{-1}$, Josien and Fuson 1952) and/or dibenzanthrone (1640 $cm^{-1}$, Durie, Lack, and Shannon 1957) similarly indicates resonance between the substituents in the 16,17-positions and the polycyclic systems.

(iv) *Evidence for 16,17-Disubstitution in the Region 900–650 $cm^{-1}$.*—In Part I of this series the absorption of I, II, and III in the aromatic CH out-of-plane region between 900 and 650 $cm^{-1}$ was discussed in some detail. In this dibenzanthrone series good correlation was found between both the positions and relative intensities of the stronger bands and the distribution of aromatic hydrogen in the molecules. The bands near 805 and 755 $cm^{-1}$ were correlated with the presence of respectively two and four adjacent aromatic CH groups on the periphery of the condensed ring system. The presence of 16,17-disubstitution in II and III resulted in a weakening of the band near 805 $cm^{-1}$ relative to the band near 755 $cm^{-1}$ owing to a reduction in the number of adjacent pairs of aromatic CH groups in these molecules. The positions and relative intensities of these bands are essentially unchanged in the spectra of IV (802, 756 $cm^{-1}$), V (803, 756 $cm^{-1}$), and VI (804, 756 $cm^{-1}$) relative to II (802, 754 $cm^{-1}$) and III (804, 758 $cm^{-1}$). This both helps to confirm the correlations and establishes that IV, V, and VI are 16,17-disubstituted dibenzanthrones. An additional feature, not discussed in Part I, which serves to distinguish the 16,17-disubstituted dibenzanthrones, is the appearance of a medium-strength band close to 730 $cm^{-1}$ in the spectra of II and III which is absent in the spectrum of I. This band is present in the spectra of IV, V, and VI.

The strong band at 695 $cm^{-1}$ in the spectra of IV, V, and VI seems to be characteristic of polynuclear quinones, since a band occurs close to this position in the spectra of all polynuclear quinones studied to date (Durie, Lack, and Shannon 1957).

* Carbonyl frequencies given in Part I of this series for II and III have now been slightly revised.

## III. Experimental

The microanalyses were made by the C.S.I.R.O. Microanalytical Laboratory and the sodium analyses by the Coal Research Section using a flame photometer. The infra-red spectra were obtained using the potassium halide disk technique with a Perkin-Elmer Model 112 recording infra-red spectrometer fitted with a rock-salt prism. The electronic spectra were measured on a Unicam SP500 spectrophotometer.

(*a*) *16-Methoxy-17-hydroxydibenzanthrone.*—16,17-Dimethoxydibenzanthrone was dissolved in concentrated sulphuric acid and the solution warmed to 60 °C. A few drops of acid solution was removed from time to time and added to excess water. When the resulting precipitate changed from green to blue, hydrolysis was assumed complete. The crude methoxyhydroxy compound was recovered by pouring the acid solution onto ice and purified by recrystallizing from nitrobenzene (Found: C, 83·4; H, 3·5; O, 12·5%. Calc. for $C_{35}H_{18}O_4$: C, 83·7; H, 3·6; O, 12·8%).

(*b*) *Sodium Salt of 16-Methoxy-17-hydroxydibenzanthrone.*—The purified quinone was boiled in alkaline aqueous dioxane or ethanol. A green salt quickly formed and was filtered and copiously washed with water, alcohol, and acetone, and dried (Found: Na, 4·4%. Calc. for $C_{35}H_{17}O_4Na$: Na, 4·4%).

(*c*) *16-Ethoxy-17-hydroxydibenzanthrone and its Sodium Salt.*—These were prepared by the above methods (Found: C, 83·9; H, 4·1; O, 12·1%. Calc. for $C_{36}H_{20}O_4$: C, 83·7; H, 3·9; O, 12·4%).

(*d*) *16-Methoxy-17-ethoxydibenzanthrone.*—The sodium salt of methoxyhydroxydibenzanthrone (0·1M) was very finely ground with anhydrous potassium carbonate (1·0M). To this was added dimethyl sulphate (0·5M) in acetone solution and the mixture boiled for 10 min. Water was added and the crude quinone filtered, dried, and recrystallized from nitrobenzene.

## IV. Acknowledgments

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# CHEMISTRY OF POLYNUCLEAR COMPOUNDS

## III. THE STRUCTURES AND ABSORPTION SPECTRA OF 1,1′-DIANTHRIMIDE AND INDANTHRONE

By R. A. Durie* and J. S. Shannon*

[*Manuscript received December* 30, 1957]

*Summary*

In an investigation into the coking mechanism of coal, polynuclear quinones have been adopted as models. The vibrational and electronic absorption spectra of indanthrone (I), 1,1′-dianthrimide (II), and 1,2,2′,1′-anthraquinoneazine (III) are presented and discussed. The absorption spectra of I and II, together with other available evidence, favour the tetraketo form rather than the enol form as recently proposed by Wyman (1956) for structure I.

### I. Introduction

As part of a programme aimed at elucidating the chemical reactions occurring during the coking of coal, the study of the pyrolytic reactions and coking of a series of polynuclear quinones is in progress. In Part I of this series (Durie, Lack, and Shannon 1957) the infra-red spectra of several polynuclear quinones were discussed; and in Part II (Durie and Shannon 1958) the behaviour in concentrated sulphuric acid of dibenzanthrone and some derivatives was examined. In the present paper the vibrational and electronic absorption spectra of indanthrone (I), 1,1′-dianthrimide (II), and 1,2,2′,1′-anthraquinoneazine (III) are considered.

The generally accepted structure for indanthrone (I) is form Ia as originally proposed by Scholl (1903), Scholl and Berblinger (1903), Scholl, Berblinger, and Mansfield (1907), and Scholl, Steinkopf, and Kabacznik (1907). However, Wyman (1956) has suggested that form Ib is more consistent with the infra-red spectra and other properties of this molecule.

Since in conjunction with the pyrolytic studies on I and II a knowledge of their structure is essential, the infra-red and electronic absorption spectra, together with other relevant evidence for I, II, and related compounds, are considered in detail below.

### II. Experimental

The infra-red spectra were obtained using the potassium halide disk technique with a Perkin Elmer Model 112 recording infra-red spectrometer fitted with either a rock-salt or a calcium fluoride prism. The electronic spectra were measured on a Unicam SP500 spectrophotometer.

### III. Results and Discussion

Table 1 gives the absorption maxima and intensities in the electronic absorption spectra of 1,1′-dianthrimide (II) and 1-aminoanthraquinone, in

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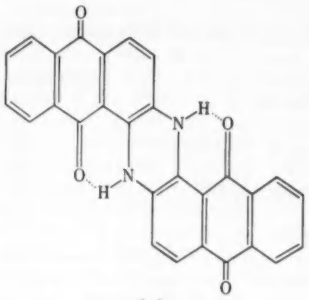
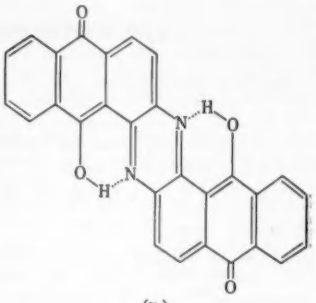
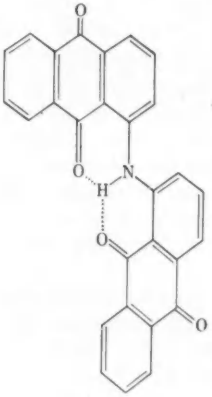


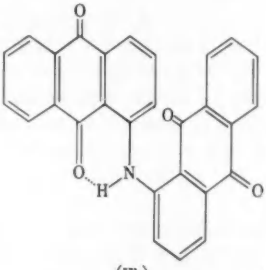
(Ia)



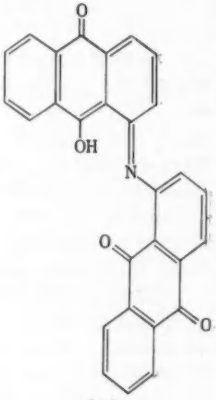
(Ib)



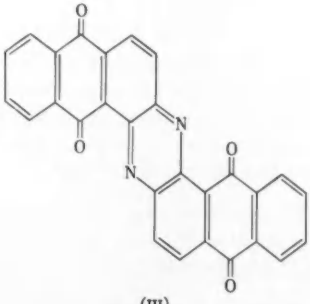
(IIa)



(IIb)



(IIc)



(III)

chlorobenzene; also of I, II, and III, and of 1-aminoanthraquinone and 1,2-diaminoanthraquinone, in concentrated sulphuric acid. The infra-red absorption spectra of I, II, and III are presented in Figure 1. A more detailed comparison of the infra-red spectra of I and II and of pyranthrone (VII) and flavanthrone (VIII) is given in Figure 2.

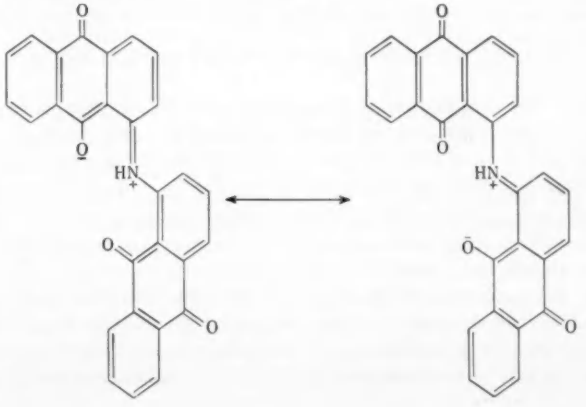
TABLE 1

ELECTRONIC ABSORPTION PEAKS

| Quinone | Chlorobenzene | Concentrated Sulphuric Acid |
|---|---|---|
| 1-Aminoanthraquinone .. .. | 463 (7200) | 378 (6000) |
| 1,1′-Dianthrimide (II) .. .. | 363 (13,400) | 368 (11,600) |
| | 516 (12,500) | |
| Indanthrone (I) .. .. .. | | 390 (7300) |
| | | 462 (10,400) |
| | | 818 (9700) |
| 1,2-2′,1′-Anthraquinoneazine (III) .. | | 414 (21,400) |
| 1,2-Diaminoanthraquinone .. .. | | 360 (6600) |

### (a) *The Structure of 1,1′-Dianthrimide (II)*

The electronic absorption spectrum of 1,1′-dianthrimide (II) in chlorobenzene displays large red shifts and increased intensities compared with the spectrum of 1-aminoanthraquinone in the same solvent (see Table 1). However, as will be clear from Table 1, these compounds have very similar spectra in concentrated sulphuric acid. These results can only be explained on the basis of an NH form for 1,1′-dianthrimide with anthraquinone moieties linked by an NH bridge. Thus the spectra in chlorobenzene indicate that resonance between the two anthraquinoyl residues involving the following type of canonical forms occurs in 1,1′-dianthrimide:



The spectra in concentrated sulphuric acid strongly suggest that protonation of the NH group of 1,1′-dianthrimide occurs in concentrated sulphuric acid as with 1-aminoanthraquinone (Durie and Shannon 1958), which inhibits resonance between the respective amino groups and their attached anthraquinoyl systems. This similarity between the spectra of the two compounds would not be expected if any other form were postulated for 1,1′-dianthrimide (e.g. form IIc). Further evidence that 1,1′-dianthrimide consists of linked anthraquinoyl moieties which

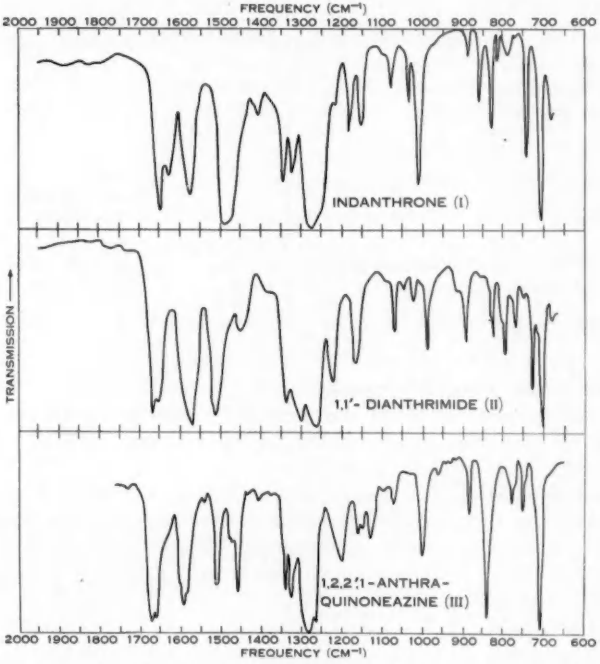



Fig. 1.—Infra-red spectra (1 per cent. of sample in 100 mg KCl disk).

are " isolated " by protonation of the amino group follows from a consideration of absorption intensities, that is, the intensity of the 368 mμ peak (ε 11,600) in the spectrum of II is approximately double that of the corresponding peak of 1-aminoanthraquinone at 378 mμ (ε 6000).

The infra-red spectrum of II shows strong bands at 1670 and 1656 $cm^{-1}$ in the region where quinonoid-carbonyl group absorption is expected to occur. Josien and Deschamps (1956) have shown that in the case of substituted *p*-quinones the number of carbonyl frequencies can be predicted from consideration of the symmetry of the molecule with respect to the quinonoid-carbonyl groups. Thus two carbonyl bands may be expected and have been observed in the case of 1-amino- and 2-aminoanthraquinones (Flett 1948 ; Durie

and Shannon, unpublished data). This non-equivalence of quinonoid carbonyl groups is due to resonance and/or hydrogen-bonding effects. In the case of 1,1′-dianthrimide (II) a *cis*-form (IIa) or a *trans*-form (IIb) is possible; two carbonyl frequencies would be expected for the *cis*-form if a bifurcated hydrogen bond structure (Nakamoto, Margoshes, and Rundle 1955) were present and three carbonyl group frequencies might be expected for the *trans*-form where only one of the inner carbonyl groups would be able to participate in hydrogen bonding with the NH group. The 1670 and 1656 $cm^{-1}$ bands in the infra-red spectrum of II can thus be assigned with some confidence to quinonoid-carbonyl group absorption. Since only two frequencies have been resolved the infra-red evidence favours slightly the *cis*-form (IIa).

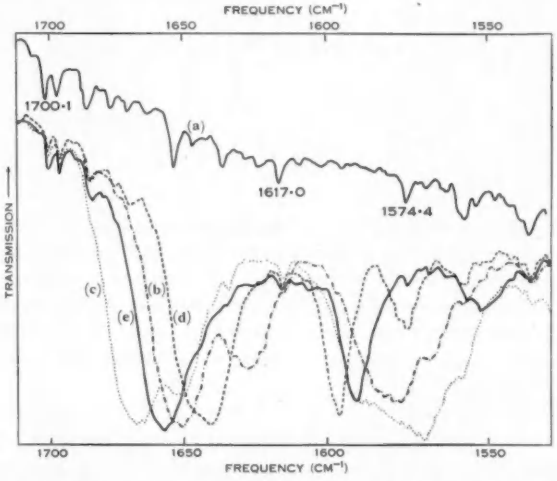



Fig. 2.—Single-beam infra-red scans (calcium fluoride prism) over region 1700–1500 $cm^{-1}$. (*a*) Background 100 mg KCl disk plus atmospheric absorption; (*b*) indanthrone (I); (*c*) 1,1′-dianthrimide (II); (*d*) pyranthrone (VII); (*e*) flavanthrone (VIII). *Note* (*b*), (*c*), and (*e*): 1 per cent. sample in 100 mg KCl disk; (*d*) 0·5 per cent. sample in 100 mg KCl disk.

The ready formation of 1,2-7,8-diphthaloylcarbazole (IV) from 1,1′-dianthrimide (Bradley and Thitchener 1953) is further support for the *cis*-form (IIa) of 1,1′-dianthrimide.

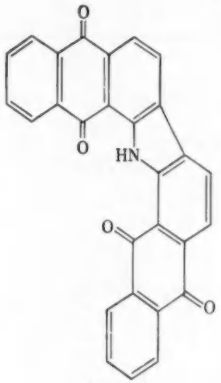
Thus the evidence considered shows that 1,1′-dianthrimide (II) has the generally accepted NH form which probably exists in the *cis*-form (IIa), the NH group being hydrogen bonded.

### (*b*) *The Structure of Indanthrone* (*I*)

The assignment of the structure of indanthrone (I) to form Ib by Wyman (1956) was based on his interpretation of the infra-red absorption spectra of I and of *N*-methylindanthrone (V), *NN*′-dimethylindanthrone (VI), and 1,2-2′,1′-

anthraquinoneazine (III). The present study of the spectra of I, II, III, and some related compounds, indicates that Wyman's conclusions are open to doubt.

(i) *NH or OH? (Form Ia or Form Ib?).*—Wyman reasons that the absence of any absorption band in the 3μ region favours the presence of OH groups (form Ib), since there is ample precedent for hydrogen-bonded OH groups failing to give discrete absorption in the infra-red but little or no evidence of NH groups behaving in this manner. The present results confirm the absence of any definitely assignable band in the NH/OH stretching-vibration region, although a weak band near 2650 $cm^{-1}$ is present in both mulls and disks of I and of 4,4′-dichloroindanthrone; this band, which is absent in the spectrum of III,




(IV)

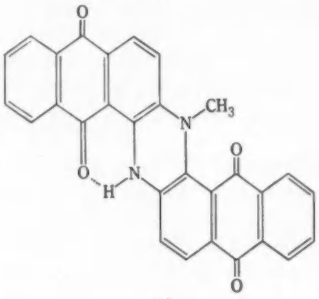
occurs outside the range of previously observed bonded NH group frequencies (Nakamoto, Margoshes, and Rundle 1955). However, in the case of II, where it has been shown that available evidence favours the NH form, no detectable absorption was observed in the NH stretching-vibration region. Thus the absence of discrete absorption in this region cannot be regarded as evidence for the absence of NH groups in I; also, if NH groups are present (form Ia), these must be participating in strong hydrogen bonding.

(ii) *Azine (=N) or NH? (Form Ib or Ia?).*—A strong band near 1585 $cm^{-1}$ in the spectrum of I was assigned to C=N absorption by Wyman on the basis of the presence of a similar strong band in the spectrum of III and its low intensity or absence in the spectra of *N*-methylindanthrone (V) and *NN*′-dimethylindanthrone (VI), since it has been established that these latter compounds, that is, V and VI, have the tetraketo form (Wyman 1956).

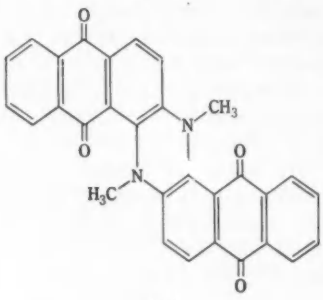
Bellamy (1954) observes that when C=N and C=C are in conjugation, particularly in cyclic systems, it is doubtful whether either group can be regarded as retaining its individual character. Thus assignment of C=N frequencies under such circumstances is not reliable. Further, pyranthrone (VII) shows more complex absorption than flavanthrone (VIII) in the 1600 $cm^{-1}$ region

of the infra-red spectrum and the former absorbs more strongly at 1600 $cm^{-1}$ than the latter (at 1594 $cm^{-1}$).

1,1′-Dianthrimide (II) and indanthrone (I) show a similar absorption pattern in the 1500–1600 $cm^{-1}$ region and II absorbs more strongly at 1575 $cm^{-1}$ than I does at 1583 $cm^{-1}$. Thus there is no precedent for assigning the 1583 $cm^{-1}$ band in the infra-red spectrum of I to a C=N vibration, and it is probably a

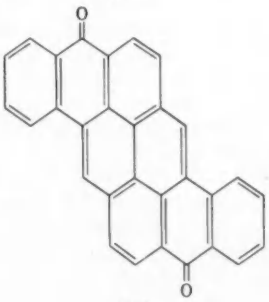


(V)

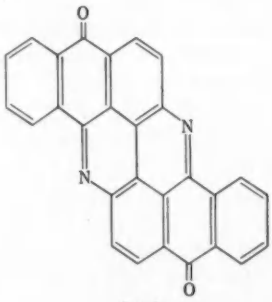


(VI)

ring vibration. It has been suggested (Durie, Lack, and Shannon 1957) that the very strong bands, that occur in this region of the infra-red spectra for all polynuclear quinones studied, may be due to the enhancement of the ring vibration absorption intensity through conjugation with the quinonoid-carbonyl groups. Consequently the infra-red absorption spectrum of I in the 1500–1600 $cm^{-1}$ region cannot be used to support an azine structure, that is, form Ib.



(VII)

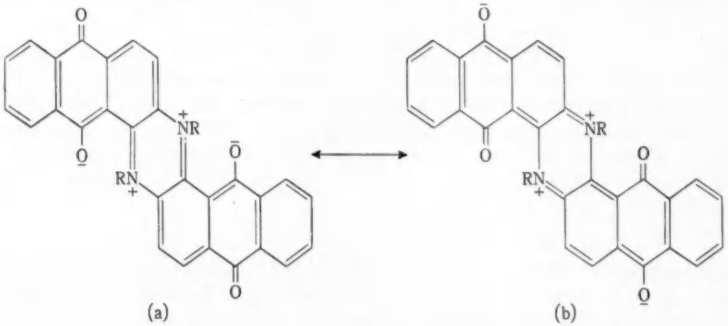


(VIII)

(iii) *Quinonoid-Carbonyl Groups : Equivalent or Non-equivalent? (Form Ib or Form Ia?).*—In the infra-red spectrum of I there is a very strong band at 1655 $cm^{-1}$, together with a pronounced peak at 1631 $cm^{-1}$ on the side of the 1655 $cm^{-1}$ band. Wyman (1956) has assigned the 1655 $cm^{-1}$ band to a quinonoid-carbonyl group frequency but the 1631 $cm^{-1}$ band, which he describes as weak, he has tentatively assigned to C=C groups. The infra-red spectra of I and II

are again very similar in the 1600–1700 $cm^{-1}$ (carbonyl) region, and each possesses a double absorption peak in this region (Fig. 2). Thus it is reasonable to assign the 1631 $cm^{-1}$ band in the spectrum of I to a second quinonoid-carbonyl frequency. In the spectrum of III in the carbonyl region there is a similar double absorption peak at 1661 and 1672 $cm^{-1}$, which, from symmetry considerations of the structure of III, may be assigned to the non-equivalent inner and outer quinonoid-carbonyl groups respectively; Wyman (1956) has again tentatively assigned the lower frequency to C=C groups. Form Ib for indanthrone has no non-equivalent quinonoid-carbonyl groups and hence only one carbonyl frequency would be expected. However, in form Ia the inner and outer quinonoid-carbonyl groups are non-equivalent and two carbonyl frequencies are to be expected. Thus the assignment of two carbonyl frequencies in the infra-red spectrum strongly supports form Ia.

The infra-red spectra of *N*-methylindanthrone (V) and *NN'*-dimethylindanthrone (VI) published by Wyman (1956) further support the assignment of two carbonyl frequencies to I. Thus in the spectrum of I there is a pronounced band at 1626 $cm^{-1}$, whereas for V there are two weaker bands near 1639 and 1626 $cm^{-1}$, also a strong 1658 $cm^{-1}$ band corresponds to the 1656 $cm^{-1}$ band in




the spectrum of I. This is consistent with the presence of three non-equivalent carbonyl groups in V due to removal of hydrogen bonding on to one of the inner carbonyl groups, which then absorbs at 1639 $cm^{-1}$ compared with 1626 $cm^{-1}$ for the bonded inner carbonyl group. In the spectrum of VI there are once more only two bands (at 1661 and 1642 $cm^{-1}$) in the carbonyl region, and only two carbonyl frequencies are expected from symmetry considerations. These changes also show that even in the absence of hydrogen bonding the inner quinonoid-carbonyl groups have a lower frequency than the outer groups, indicating that canonical forms of type (a) contribute more to the resonance hybrids of I, V, and VI than do forms of type (b).

A comparison of the electronic absorption spectra in concentrated sulphuric acid of I and 1,2-diaminoanthraquinone provides further evidence of this amide type resonance in I. In concentrated sulphuric acid I absorbs at longer wavelengths than 1,2-diaminoanthraquinone and 1,2-diaminoanthraquinone absorbs at longer wavelengths in chlorobenzene than in concentrated sulphuric acid.

Thus it is evident that protonation of the amino nitrogen occurs in the case of 1,2-diaminoanthraquinone in sulphuric acid (Durie and Shannon 1958), but strong amide type resonance in I persists in concentrated sulphuric acid and inhibits protonation of the NH groups.

Amide resonance has already been postulated to explain the absorption spectrum of 1,1′-dianthrimide (II) in chlorobenzene. However, for II, unlike I, contribution of this type of resonance is not sufficiently strong for it to prevent protonation of the NH group in concentrated sulphuric acid. A comparison of the infra-red carbonyl frequencies of I, II, III, and anthraquinone is of considerable interest with respect to this effect, and the structure of I. The high-frequency carbonyl group absorption in the infra-red spectra of II (1670 $cm^{-1}$) and III (1672 $cm^{-1}$) is not much lower than the frequency of the carbonyl band in the spectrum of anthraquinone (1675 $cm^{-1}$). This shows that no extensive conjugation occurs through the NH bridge in the case of II or through the azine ring in the case of III. On the other hand, for I the higher carbonyl frequency falls to 1655 $cm^{-1}$, suggesting that extensive conjugation does occur between the anthraquinone moieties of I. Thus the evidence suggests a more highly conjugated structure for I than for II and III, which would be expected if I had the structure Ia but not if it had the structure Ib. Also on this basis it is not difficult to understand the large differences between the electronic absorption spectra of I and of III, since I would then be expected to absorb at longer wavelengths and hence be more highly coloured than III, as is in fact the case.

As a broad generalization, the lowering of carbonyl group frequencies by conjugative-chelation type hydrogen bonding is accompanied by a significant increase in the intensity of the carbonyl group absorption. Thus with the enolic form of β-diketones (Rasmussen, Tunnicliff, and Brattain 1949) and β-keto esters (Leonard *et al.* 1952) the low-frequency chelated carbonyl group absorption is considerably more intense than the keto-form carbonyl absorption. Also, in the spectrum of the hydrogen-bonded 1,8-dihydroxyanthraquinone, the low-frequency quinonoid-carbonyl band is stronger than the high-frequency quinonoid-carbonyl band (Durie and Shannon, unpublished data). The increase in carbonyl group absorption intensity appears to be related to the extent of the shift to lower frequencies. Thus it has been suggested (Rasmussen, Tunnicliff, and Brattain 1949) that in the chelated form there occurs a greater decrease in the carbonyl bond order than would be given by simple conjugation, and an increase in the charge on the carbonyl oxygen due to a greater contribution of charged resonance structures. In the published spectra of I, V, and VI (Wyman 1956) no outstanding changes are evident in the carbonyl group absorption intensities when conditions favour hydrogen-bond formation as in I and V; however, in V the band near 1626 $cm^{-1}$ is more pronounced than the band near 1639 $cm^{-1}$; and the 1626 $cm^{-1}$ band in I is somewhat broader than the band near 1642 $cm^{-1}$ in V. These changes are consistent with the general effect of hydrogen bonding on carbonyl group absorption intensities and thus lend some additional support to the carbonyl group frequency assignments that have been made in the spectrum of I.

The two peaks at 1655 and 1631 $cm^{-1}$ for indanthrone (I) are both shifted to higher frequencies, namely 1663 and 1638 $cm^{-1}$, in 4,4′-dichloroindanthrone (Durie and Shannon, unpublished data). This observation is consistent with the expected effect on the quinonoid-carbonyl frequency of electronegative substituents (Durie, Lack, and Shannon 1957), and thus provides further justification for the assignment of two carbonyl frequencies in the spectrum of I.

Appleton and Geake (1941) have obtained evidence for the existence of two vats* for *N*-methylindanthrone as well as 1,2′-dianthrimide, 1,2-7,8-diphthaloylcarbazole (IV), and 2-benzoylaminoanthraquinone. These authors attribute this behaviour to the formation of intermediate di-semiquinones which are strongly resonance stabilized, and it was suggested that the blue vat of indanthrone is of this type. Thus the formation of two vats by I is not inconsistent with form Ia.

Kuhn (1932) originally proposed a charged structure for indanthrone (I) to explain the behaviour of this molecule. However, in the light of modern resonance theory it is more likely that I is a resonance hybrid of a large number of contributing charged structures. Gill and Stonehill (1944) have proposed a resonance hybrid of forms Ia and Ib. This is unlikely in view of the modern theory of the electrostatic nature of the hydrogen bond (Coulson 1957); also a wider separation of the carbonyl frequencies might be expected if this proposed structure for I were correct.

Thus all the evidence considered favours the generally accepted form Ia for indanthrone, and the postulation of amide-type resonance in form Ia may account for the properties of this molecule.

## IV. Acknowledgments

The quinones used as starting material were a generous gift from Imperial Chemical Industries, Ltd. (Dyestuffs Division), England. The authors are grateful for support and encouragement received from Mr. H. R. Brown, Officer-in-Charge, Coal Research Section, C.S.I.R.O., during the course of the researches and in the preparation of the paper. They wish to thank Mr. J. D. Brooks for his interest and helpful suggestions, and Mrs. A. Jackson and Mrs. O. V. Molnar for technical assistance.

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* The term "vat" refers to the coloured solution of a reduced vat dye (leuco-compound) in alkaline hydrosulphite solution.

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# ARYLATION OF AROMATIC COMPOUNDS*

## VI. BENZOYL PEROXIDE WITH PYRIDINE AND QUINOLINE

By K. H. PAUSACKER†

[*Manuscript received December* 10, 1957]

*Summary*

Amongst the products formed when pyridine reacts with benzoyl peroxide are phenylpyridines, benzoic acid, pyridine oxide, and dipyridyls. The molar yield of benzoic acid is significantly higher than that of the phenylpyridines although most aromatic compounds give approximately equal yields of benzoic acid and phenylated compounds. This difference may be ascribed to the simultaneous formation of pyridine oxide and dipyridyls. Similar remarks apply to the reaction with quinoline and the mechanisms of the various reactions are discussed.

The phenylquinoline fraction has been investigated in detail and the isomer ratio of the mixture has been evaluated.

## I. INTRODUCTION

The reaction of pyridine with a number of substituted benzoyl peroxides has been studied (Hey and Walker 1948; Hey, Stirling, and Williams 1955) but a complete assessment of all the products has not been made. However, it is interesting to note, that in all cases the molar yield of the corresponding benzoic acid (when isolated) is much greater than the yield of the arylpyridines. The highest yields of acid were obtained when *o*-, and *m*-nitrobenzoyl peroxides react with pyridine (1·73 and 1·80 mol of acids respectively). In previous Parts of this series (Lynch and Pausacker 1957*a*, 1957*b*; Pausacker 1957; Karelsky and Pausacker 1958) it has been found that the molar yield of benzoic acid has always been less than unity and it will be shown why this value is greater than unity when pyridine and quinoline are used.

The composition of the phenylpyridines formed during the reaction of benzoyl peroxide with pyridine has been established (Hey, Stirling, and Williams 1955) to be 54 per cent. 2-, 32 per cent. 3-, and 14 per cent. 4-phenylpyridine and these yields have been shown to be in agreement with theoretical calculations (Brown 1956). There is only one report (Hey and Walker 1948) of the reaction of quinoline with benzoyl peroxide and the phenylquinoline fraction has been only partly resolved. 4-Phenylquinoline (7 per cent.) and 5-phenylquinoline (trace) were isolated by fractional crystallization of the picrates. In the present paper, an attempt has been made to resolve the phenylquinoline fraction into all its components. The results obtained are not in agreement with the predictions made by Sandorfy and Yvan (1950) on the basis of theoretical calculations.

* For Part V of this series see Karelsky and Pausacker (1958).

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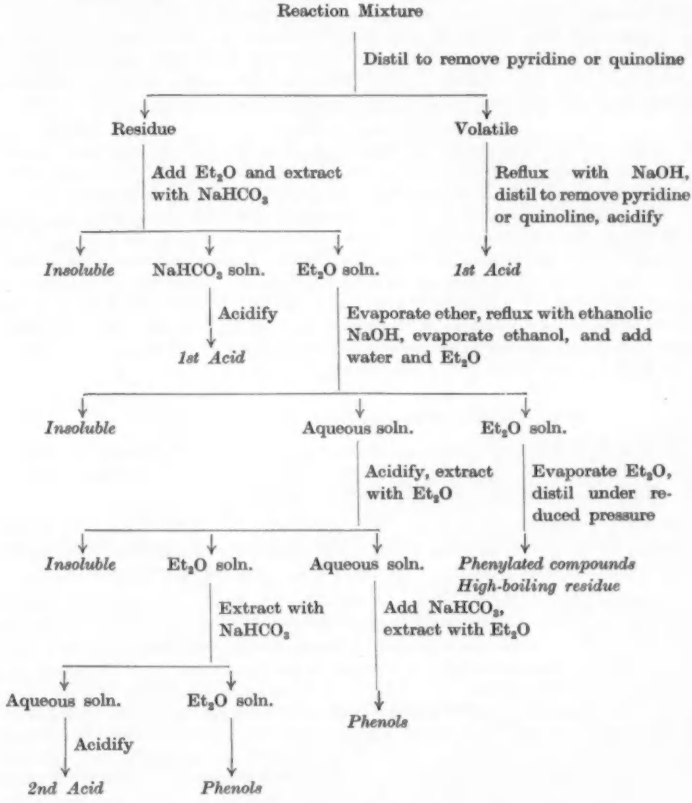
## II. Experimental

### (a) *Reagents*

Benzoyl peroxide was purified as described in Part I of this series (Lynch and Pausacker 1957*a*) and pyridine (B.D.H., Analar grade) and quinoline (synthetic) were distilled immediately prior to use.

### (b) *General Procedure*

Reactions were carried out in the apparatus already described (Lynch and Pausacker 1957*a*). In each experiment, benzoyl peroxide (20 g) and either pyridine or quinoline (300 ml) were heated at 100 °C for 5 hr. The various products were separated as shown in the following flow sheet:




### (c) *Reaction of Benzoyl Peroxide with Pyridine*

(i) *General Remarks.*—The reaction mixture rapidly darkened and the evolution of carbon dioxide ceased after about 1 hr. In preliminary experiments at 78 °C, it was noted that there was an induction period (*c.* 20 min) before the rapid evolution of carbon dioxide.

(ii) *Yields of Products.*—Several runs were performed and good agreement was obtained. The average yields of the various products were as follows (the values in parentheses represent the yield in mol per mol of benzoyl peroxide): carbon dioxide, 1460 ml (0·80); 1st acid, 10·75 g

(1·08); 2nd acid, 1·35 g (0·14); phenylpyridines, 7·4 g (0·58); phenols, 0·30 g (0·04); insoluble, 0·60 g; high-boiling residue, 1·1 g.

(iii) *Phenylpyridines.*—The fraction, b.p. 141–144 °C/11 mm, was collected (Found: C, 85·2; H, 5·9; N, 9·4%. Calc. for $C_{11}H_9N$: C, 85·2; H, 5·8; N, 9·0%). A small amount was dissolved in ethanol and added to an aqueous solution of ferrous sulphate. A rose-red colour, similar to that obtained with αα′-dipyridyl, was observed.

(iv) *High-Boiling Residue.*—This was a brown crystalline mass (Found: C, 85·5; H, 5·6; N, 7·4%). It was crystallized from benzene, and the solid obtained was further crystallized from ethanol to give fine, white needles, m.p. 239 °C (Found: C, 85·7; H, 5·4; N, 8·9%; mol. wt. (Rast), 286. Calc. for $C_{22}H_{16}N_2$: C, 85·7; H, 5·2; N, 9·1%; mol. wt., 308). The benzene filtrate was evaporated and the residue was sublimed at 180–230 °C/0·05 mm. The sublimate crystallized from ethanol as pale, yellow needles, m.p. 208 °C, mixed m.p. with m.p. 239 °C compound, 220–228 °C (Found: C, 85·7; H, 5·1; N, 8·9%; mol. wt. (Rast), 304. Calc. for $C_{22}H_{16}N_2$: C, 85·7; H, 5·2; N, 9·1%; mol. wt., 308). Both compounds, m.p.'s 208 and 239 °C, gave a faint pink colour when ethanolic solutions were added to aqueous ferrous sulphate.

(v) *Isolation of Pyridine Oxide.*—In one experiment, the pyridine was first evaporated, the residue was dissolved in chloroform (100 ml) and anhydrous sodium carbonate (20 g) was added. After standing for several hours, the solid was filtered and, after treatment with dilute sulphuric acid, yielded benzoic acid (11·45 g). The filtrate was distilled and two fractions (*a*) b.p. 147–150 °C/13 mm, 5·0 g (Found: C, 82·5; H, 6·1; N, 8·7%); and (*b*) b.p. 150–151 °C/13 mm, 3·6 g (Found: C, 81·7; H, 5·8; N, 8·5%) were collected. The residue weighed 2·4 g. Fractions (*a*) and (*b*) were combined and extracted with 3×5 ml water. The combined aqueous extracts were added to a solution of picric acid (2 g) in water (100 ml) and the solid (0·90 g), which precipitated on standing, was filtered. It crystallized from ethanol as pale yellow needles, m.p. (and mixed m.p. with pyridine oxide picrate) 179 °C (Found: C, 40·9; H, 2·6; N, 17·2%. Calc. for $C_{11}H_8N_4O_8$: C, 40·7; H, 2·5; N, 17·3%).

### (*d*) *Reaction of Benzoyl Peroxide with Quinoline*

(i) *General Remarks.*—The appearance of the reaction mixture was similar to that already noted with pyridine. An induction period of 15–20 min was noted. When reaction was attempted at 78 °C, no carbon dioxide had been evolved after 6 hours' heating.

(ii) *Yields of Products.*—The average yields obtained in concordant runs were as follows: carbon dioxide, 868 ml (0·47); 1st acid, 10·8 g (1·08); 2nd acid, 4·9 g (0·49); phenylquinolines, 6·1 g (0·36); phenols, 2·15 g (0·18); insoluble, 1·0 g; high-boiling residue, 3·3 g.

(iii) *Phenylquinolines.*—The fraction, b.p. 124–134 °C/0·08 mm, was collected. At first it was considered that the isomer-ratio could possibly be determined by U.V. analysis of the mixture and for this purpose the seven possible phenylquinolines were obtained as follows: 2-phenylquinoline (m.p. 82 °C) was prepared by the reaction of quinoline with phenylmagnesium bromide (Gilman and Gainer 1949), picrate m.p. 190 °C. 3-Phenylquinoline (b.p. 175 °C/0·5 mm) was prepared by the reaction of *o*-aminobenzaldehyde with phenylacetaldehyde (Friedlander and Gohring 1883), picrate m.p. 207 °C. 4-Phenylquinoline (b.p. 156 °C/0·3 mm) was prepared by the reaction of β-chloropropriophenone with aniline (Kenner and Statham 1935), picrate m.p. 224 °C. 5-Phenylquinoline (m.p. 81 °C) was obtained from its picrate (m.p. 210 °C) which was kindly supplied by Dr. F. H. Case (1951). 6-Phenylquinoline (m.p. 110 °C) was kindly supplied by Dr. C. E. Kaslow (Kaslow and Hayek 1951), picrate m.p. 202 °C. *7-Phenylquinoline* was prepared by means of a Skraup reaction from *m*-aminodiphenyl (Hey and Walker 1948). It was separated from the 5-phenylquinoline simultaneously formed by the relative insolubility of its picrate (m.p. 213 °C) in ethanol. The picrate was converted into the free base (b.p. 158–161 °C/0·3 mm), using lithium hydroxide (Found: C, 87·9; H, 5·2; N, 7·1%. Calc. for $C_{15}H_{11}N$: C, 87·8; H, 5·4; N, 6·8%). 8-Phenylquinoline (b.p. 163 °C/0·3 mm) was kindly supplied by Dr. C. E. Kaslow. Its picrate crystallized from ethanol, m.p. 153 °C (Found: C, 58·1; H, 3·4; N, 12·9%. Calc. for $C_{21}H_{14}O_7N_4$: C, 58·0; H, 3·2; N, 12·9%). Hey and

Walker (1948) have claimed that this picrate melts at 200 °C but Avramoff and Sprinzak (1957) have recently stated that its m.p. is 154 °C.

The ultraviolet spectra of 2-, 3-, 4-, 5-, 6-, 7-, and 8-phenylquinolines were measured in both ethanol and 0·1N hydrochloric acid by Miss Margarita Karelsky. The results are shown in Table 1. It is seen that there is a marked similarity between these various spectra and so the presence of any particular compound in the phenylquinoline mixture could not be detected with certainty.

Paper chromatography was next used in order to separate the mixture. When 80% *n*-butanol : 17% water : 3% acetic acid, 80% *n*-propanol : 10% formic acid : 10% water, and 80% *n*-butanol : 10% trichloroacetic acid : 10% water were used, the $R_F$ values of all the compounds were very close to unity and, with 3% aqueous ammonium chloride, all $R_F$ values were zero.

TABLE 1

ULTRAVIOLET ABSORPTION SPECTRA OF 2-, 3-, 4-, 6-, 7-, AND 8-PHENYLQUINOLINES

| Substituent | In Ethanol | | | | In 0·1N Hydrochloric Acid | | | |
|---|---|---|---|---|---|---|---|---|
| | $\lambda_{max.}$ (mμ) | ε | $\lambda_{min.}$ (mμ) | ε | $\lambda_{max.}$ (mμ) | ε | $\lambda_{min.}$ (mμ) | ε |
| Phenylquinolines | | | | | | | | |
| 2- .. .. | 256 | 4·50 | 232 | 3·85 | 208 | 4·50 | 223 | 3·93 |
| | 322 | 3·85 | 300 | 3·80 | 238 | 4·32 | 252 | 4·12 |
| | | | | | 269 | 4·35 | 287 | 3·30 |
| | | | | | 338 | 4·32 | | |
| 3- .. .. | 253 | 4·50 | | | 250 | 4·45 | 229 | 3·84 |
| | | | | | 335 | 3·66 | 305 | 3·40 |
| 4- .. .. | 227 | 4·56 | 259 | 3·66 | 238 | 4·55 | 220 | 4·09 |
| | 295 | 3·91 | | | 316 | 4·05 | 260 | 3·20 |
| 6- .. .. | 253 | 4·64 | 225 | 4·18 | 263 | 4·53 | 226 | 4·04 |
| | | | | | 325 | 3·78 | 292 | 3·52 |
| 7- .. .. | 252 | 4·60 | | | 235 | 4·90 | 292 | 3·53 |
| | | | | | 325 | 4·38 | | |
| 8- .. .. | 233 | 4·50 | 267 | 3·60 | 240 | 4·53 | 225 | 4·25 |
| | 300 | 3·80 | | | 315 | 3·80 | 280 | 3·15 |

The best results were obtained with 20% dimethylformamide : 80% aqueous ammonium chloride (3%) when the front of the spots had $R_F$ values of 0·5–0·8. The spots were rather large and could not be used for quantitative separation but, when viewed under ultraviolet light, the fluorescent appearance of each spot allowed a qualitative identification. Their appearance and $R_F$ values are as follows: 2-, very dull blue with long tail, 0·51; 3-, dull blue, 0·61; 4-, dull blue, 0·73; 5-, bright yellow, 0·76; 6-, dull blue with long tail, 0·65; 7-, very bright blue, 0·68; 8-, dull yellow, 0·83. Although an actual separation could not be achieved by paper chromatography, this technique can be used for the qualitative determination of these compounds in certain mixtures.

However, adsorption chromatography on alumina led to a partial separation of the components. The phenylquinoline fraction (5·3 g) was dissolved in light petroleum (b.p. 60–80 °C) and eluted with the various solvents shown in Table 2. The eluant was changed whenever less than 0·06 g of material was eluted in a fraction.

TABLE 2

CHROMATOGRAPHY OF PHENYLQUINOLINES ON ALUMINA

Fractions: 1, solid; 2–6, oily solids; 7–38, yellow oils; 39–51, whitish oils; 52–61, oily solids; 62–64, yellow oils. The solid in fraction 1 was proved to be identical with 2-phenylquinoline (m.p. and mixed m.p. with an authentic sample, 82 °C)

| Fraction Numbers | Eluant | Volume of Each Fraction (ml) | Weight Eluted (g) |
|---|---|---|---|
| 1 | Light petroleum* | 300 | 0·144 |
| 2–9 | Light petroleum | 70 | 0·639 |
| 10–20 | Light petroleum | 300 | 1·118 |
| 21–24 | Light petroleum | 600 | 0·270 |
| 25–30 | 5% $C_6H_6$/95% L.P. | 70 | 0·117 |
| 31–32 | 5% $C_6H_6$/95% L.P. | 300 | 0·203 |
| 33–37 | 10% $C_6H_6$/90% L.P. | 300 | 0·397 |
| 38–43 | 20% $C_6H_6$/80% L.P. | 300 | 0·501 |
| 44 | 50% $C_6H_6$/50% L.P. | 200 | 0·249 |
| 45 | 50% $C_6H_6$/50% L.P. | 150 | 0·145 |
| 46–47 | 50% $C_6H_6$/50% L.P. | 70 | 0·080 |
| 48–55 | 50% $C_6H_6$/50% L.P. | 300 | 0·781 |
| 56–60 | $C_6H_6$ | 300 | 0·418 |
| 61–63 | 99% $C_6H_6$/1% $C_2H_5OH$ | 300 | 0·218 |
| 64 | $C_2H_5OH$ | 300 | 0·039 |

* Refers to light petroleum (L.P.), b.p. 60–80 °C.

Selected fractions were then chosen and were examined by (*a*) determination of m.p. when solid or (*b*) conversion into the picrate which was fractionally crystallized from ethanol. These results are summarized in Table 3. The pure picrates were also mixed in approximately equal proportions and the m.p.'s were recorded (see Table 4).

TABLE 3

INVESTIGATION OF SELECTED FRACTIONS FROM THE CHROMATOGRAPHY OF PHENYLQUINOLINES

| Fraction Number | Weight (g) | Picrates | Major Compounds |
|---|---|---|---|
| 5 | 0·087 | 85% m.p. 148 °C, mixed m.p. with 8-, 152 °C | 2-, 8- |
| 10 | 0·220 | 83% m.p. 144 °C, mixed m.p. with 8-, 148 °C | 8- |
| 19 | 0·052 | 70% m.p. 130 °C, mixed m.p. with 8-, 136 °C<br>30% m.p. 190 °C, depressed with 2-, 3-, 6-, and 7-, mixed m.p. with 4-, 220 °C; mixed m.p. with 5-, 202 °C | 8-, 4-, 5- |
| 23 | 0·081 | 20% m.p. 120 °C, mixed m.p. with 8-, 130 °C<br>80% m.p. 198 °C, depressed with 3-, 6-, 7-, mixed m.p. with 4-, 218 °C, mixed m.p. with 5-, 200 °C | 4-, 5-, 8- |

TABLE 3 (*Continued*)

| Fraction Number | Weight (g) | Picrates | Major Compounds |
|---|---|---|---|
| 32 | 0·123 | 30% m.p. 208 °C, depressed with 3-, 4-, 6-, 7-, mixed m.p. with 5-, 210 °C<br>70% m.p. 206 °C, depressed with 3-, 5-, 6-, 7-, mixed m.p. with 4-, 224 °C | 4-, 5- |
| 37 | 0·058 | m.p. 196–204 °C, depressed with 3-, 6-, 7-, mixed m.p. with 5-, 198 °C ; mixed m.p. with 4-, 220 °C | 4-, 5- |
| 39 | 0·095 | 30% m.p. 183 °C, depressed with 5-, 6-, 7-, mixed m.p. with 3-, 186 °C ; mixed m.p. with 4-, 186 °C<br>70% m.p. 191 °C, depressed with 5-, 6-, 7-, mixed m.p. with 3-, 194 °C, mixed m.p. with 4-, 206 °C | 4-, 3- |
| 43 | 0·067 | 80% m.p. 200 °C, depressed with 5-, 6-, 7-, mixed m.p. with 3-, 203 °C, mixed m.p. with 4-, 205 °C<br>20% m.p. 195 °C, depressed with 3-, 6-, 7-, mixed m.p. with 4-, 215 °C ; mixed m.p. with 5-, 198 °C | 3-, 4-, 5- |
| 44 | 0·249 | 80% m.p. 203 °C, depressed with 5-, 6-, 7-, mixed m.p. with 3-, 204 °C ; mixed m.p. with 4-, 210 °C<br>20% m.p. 192 °C, depressed with 3-, 6-, 7-, mixed m.p. with 4-, 216 °C ; mixed m.p. with 5-, 206 °C | 3-, 4-, 5- |
| 48 | 0·149 | m.p. 192 °C, depressed with 6-, 7-, mixed m.p. with 3-, 196 °C ; mixed m.p. with 4-, 210 °C ; mixed m.p. with 5-, 196 °C | 3-, 4-, 5- |
| 52 | 0·083 | 20% m.p. 196 °C, depressed with 3-, 4-, 5-, 6-, mixed m.p. with 7-, 204 °C<br>80% m.p. 166 °C | 7-, + |
| 55 | 0·063 | m.p. 174 °C | |
| 57 | 0·133 | This fraction was not converted into its picrate but was crystallized from light petroleum, b.p. 40–60 °C, to give 0·070 g 6-phenylquinoline, m.p. 104 °C, mixed m.p. 105 °C | 6- |

TABLE 4

MELTING POINTS (°C) OF MIXTURES OF THE PICRATES OF THE VARIOUS PHENYLQUINOLINES

| Phenylquinolines | 3- | 4- | 5- | 6- | 7- |
|---|---|---|---|---|---|
| 3- | 207 | 204 | 189 | 184 | 193 |
| 4- | | 224 | 197 | 185 | 191 |
| 5- | | | 210 | 182 | 185 |
| 6- | | | | 202 | 183 |
| 7- | | | | | 213 |

It is seen that each of the seven possible phenylquinolines (or their picrates) have been isolated. A reasonably clean separation of 2-, 8-, and 6-phenylquinoline has been effected and the order of elution appears to be $2>8>5\simeq4\simeq3>6\simeq7$. On the basis of the weight of each fraction eluted, and the m.p.'s of the picrates, it is possible to assess the composition of the phenylquinoline fraction as follows: 2-, 6%; 3-, 14%; 4-, *c.* 20%; 5-, *c.* 12%; 6-, 8%; 7-, 8%; 8-, 30%. It is hoped to examine further this mixture by vapour-phase chromatography.

(iv) *High-Boiling Residue.*—After the phenylquinolines had been removed, a second fraction (2 g) was obtained b.p. 182–190 °C/0·12 mm (Found: C, 85·4; H, 5·2; N, 8·3%). A permanganate colour was obtained when a portion of this material was dissolved in ethanol and added to cuprous chloride in hydrochloric acid. A similar colour was observed when αα′-diquinolyl (kindly donated by Dr. W. H. F. Sasse) interacted with cuprous chloride. The residue (1·1 g) could not be distilled (Found: C, 81·2; H, 5·5; N, 6·6%).

## III. Discussion

Perhaps one of the most interesting features of the reaction of pyridine and quinoline with benzoyl peroxide is the fact that the molar yield of 1st benzoic acid is much greater than that of the phenylated compounds. This has been noted previously (Augood and Williams 1957*c*) and has also been discussed in Section I.

It would be possible to explain this high yield of 1st benzoic acid if diaryl formation occurred as follows:

$$2ArH+(PhCO_2)_2\rightarrow Ar\cdot Ar+2Ph\cdot CO_2H.$$

In the reaction of pyridine with benzoyl peroxide, it has now been found that the so-called phenylpyridine fraction gives a rose-red colour with ferrous sulphate. It is difficult to see how this colour could arise from any compound other than αα′-dipyridyl, which would distil with the phenylpyridines. Although part of the excess 1st benzoic acid may be explained by dipyridyl formation, this can only account for a relatively small amount as the elemental analysis of the phenylpyridine fraction indicates that little dipyridyl can be present.

When quinoline reacted with benzoyl peroxide there was an appreciable amount of material obtained whose boiling point was higher than that of the phenylquinolines and which, moreover, gave a colour reaction with cuprous chloride similar to that given by αα′-diquinolyl. In addition, this fraction has a value for the nitrogen analysis (8·3 per cent.) which is considerably higher than that for phenylquinoline (6·8 per cent.). It is assumed that this is a mixture of approximately equal parts (by weight) of diphenylquinolines (N=5·0 per cent.) and diquinolyls (N=10·9 per cent.). This corresponds to 0·04 mol of diphenylquinolines and 0·05 mol of diquinolyls.

Thus positive evidence has been obtained that diaryls can be formed in small yield when both pyridine and quinoline react with benzoyl peroxide. As this has never been noted previously (Augood and Williams 1957*b*), it is of interest to see why diaryl formation can occur in these cases. The fact that most aromatic compounds (ArH) do not yield diaryls (Ar·Ar) has been used as

evidence (Augood and Williams 1957*a*) that the radical Ar· is never formed during the phenylation reaction, which is presumed to occur as follows:

$$(PhCO_2)_2 \rightarrow PhCO_2 \rightarrow Ph + CO_2,$$
$$Ph + ArH \rightarrow PhArH,$$
$$PhArH + PhCO_2 \rightarrow PhAr + PhCO_2H.$$

The formation of dipyridyl (and diquinolyl) is probably due to the participation of the following reactions which are similar to those postulated by Horner (1955) for the reaction of tertiary amines with benzoyl peroxide.

$$C_5H_5N: + (PhCO_2)_2 \rightarrow C_5H_5N\cdot^+ + PhCO_2^- + PhCO_2\cdot,$$
$$C_5H_5N\cdot^+ + PhCO_2^- \rightarrow C_5H_4N\}\cdot + PhCO_2H,$$
$$2C_5H_4N\}\cdot \rightarrow (C_5H_4N)_2.$$

One other way in which the molar yield of 1st benzoic acid could be raised is that the various reaction products could become arylated further. This has been discussed for the reaction of benzoyl peroxide with benzene (Lynch and Pausacker 1957*a*) and evidence has already been presented above for the formation of diphenylquinolines. In addition it may be noted that the high-boiling residue in the reaction with pyridine has a nitrogen analysis (7·4 per cent.) intermediate between those for phenylpyridines (N = 9·0 per cent.) and diphenylpyridines (N = 6·1 per cent.). The amount of benzoic acid formed during these further phenylations would still not be sufficient to account for the excess noted.

Now it has been shown that pyridine oxide can be isolated from the reaction of pyridine with benzoyl peroxide and doubtless quinoline oxide is formed from quinoline. The overall equation for the formation of pyridine oxide is assumed to be as follows:

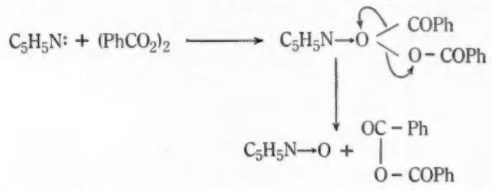
$$C_5H_5N + (PhCO_2)_2 \rightarrow C_5H_5NO + (PhCO)_2O.$$

This is analogous to the reaction of benzoyl peroxide with tertiary phosphines to form phosphine oxides and benzoic anhydride (Denney and Greenbaum 1957) and with sulphides to form sulphoxides and benzoic anhydride (Horner and Jurgens 1957).

This reaction would not be expected to lead to an increase in the 1st benzoic acid, however, for in previous papers (Lynch and Pausacker 1957*a*, 1957*b*) it has been assumed that benzoic anhydride ultimately appears as 2nd benzoic acid. Independent experiments showed that when commercial benzoic anhydride is dissolved in ether, very little benzoic acid (9 per cent.) is extracted with aqueous sodium bicarbonate. Benzoic anhydride was also heated with pyridine, under the conditions used in the reaction with benzoyl peroxide, and the pyridine was distilled. When the residue was dissolved in ether, a high yield of benzoic acid (90 per cent.) was extracted with aqueous sodium bicarbonate. Thus pyridine has converted benzoic anhydride into an intermediate which is readily transformed to benzoic acid. For this reason the 1st benzoic acid will increase by 2 mol per mol of pyridine oxide formed. Some idea of the yield of pyridine oxide can be obtained from the results quoted in Section II (*c*) (v). The elemental analysis of fraction (*a*) corresponds to approximately 88 per cent. phenylpyridine:

6 per cent. benzoic acid : 6 per cent. pyridine oxide and that of fraction (*b*) to 80 per cent. phenylpyridine : 10 per cent. benzoic acid : 10 per cent. pyridine oxide. This means that at least 0·66 g (0·09 mol) pyridine oxide is formed, which is quite appreciable compared with the yield of phenylpyridines (0·58 mol).

Both Horner (1955) and Imoto and Takemoto (1956) have stated that benzoyl peroxide initially forms a complex with tertiary amines and, on the basis of Imoto and Takemoto's structure for this complex, it would appear that the mechanism of pyridine oxide formation may be written as follows :




This mechanism shows some similarity with that proposed for the reaction of perbenzoic acid with olefins (Lynch and Pausacker 1955). In this latter work, it was found that perbenzoic acids containing electron-attracting substituents oxidized olefins more rapidly than perbenzoic acid itself. It is therefore reasonable to assume that benzoyl peroxides containing electron-attracting substituents would facilitate *N*-oxide formation. This appears to be borne out by the fact that both *o*- and *m*-nitrobenzoyl peroxides give such a high yield of 1st acid (Hey and Walker 1948). The authors remark that pyridine oxide may be formed in these reactions but no attempt was made to isolate it.

Pyridine has frequently been used in " competitive arylation " experiments (see Augood and Williams 1957*b*, for relative references) but little account has been taken of these various competing reactions that occur simultaneously. This would mean that the reactivity of pyridine, relative to that of benzene, should be greater than the value of 1·04 quoted by Augood, Hey, and Williams (1952). Dannley and Gregg (1954), in a more detailed study at a different concentration, stated that the relative reactivity of pyridine is 1·5, but they did not consider the simultaneous formation of pyridine oxide. In this regard it is interesting to note that Nozaki and Bartlett (1946) have found that benzoyl peroxide is 77·3 per cent. decomposed in pyridine, whereas it is only 15·5 per cent. decomposed in benzene under the same conditions. On the basis of reactions with acetyl peroxide, Levy and Szwarc (1954) claim that the relative reactivity of pyridine is 3.

It is also of interest to note (Section II (*c*) (iii)) that compounds of the type, $C_6H_5 \cdot C_5H_3N \cdot C_5H_3N \cdot C_6H_5$, are formed during the reaction with pyridine. This is similar to the formation of quaterphenyl from the reaction of benzoyl peroxide with benzene (Lynch and Pausacker 1957*b*) and of disubstituted quaterphenyls from substituted benzoyl peroxides and benzene (Pausacker 1957).

In the reaction of benzoyl peroxide with quinoline, it has been found that the phenylquinoline fraction consists of a mixture of 2- (6 per cent.), 3- (14 per

cent.), 4- (*c.* 20 per cent.), 5- (*c.* 12 per cent.), 6- (8 per cent.), 7- (8 per cent.), and 8- (30 per cent.) phenylquinolines. Now it is generally assumed that the position of substitution in free radical attack is determined by the localization energy (Szwarc 1957) and calculations made by Sandorfy and Yvan (1950) indicate that the position of substitution of quinoline should be 4->5->8->2->6-=7->3-. It is obvious that the experimental results are not in accord with those derived theoretically and it would therefore be of interest if Brown's (1956) method of treatment of pyridine could be applied to quinoline. The fact that all possible phenylquinolines have apparently been formed is not surprising in view of the high reactivity of the phenyl radical (Eisch and Gilman 1957), which is therefore not very selective. It is hoped to examine the reaction of quinoline with a less reactive radical in the future.

It has also been found that the yield of phenols is much higher, and that of carbon dioxide is much lower, with quinoline than with pyridine. This indicates (Lynch and Pausacker 1957*b*; Karelsky and Pausacker 1958) much greater reactivity of quinoline towards radical attack and may be compared with the similar results obtained when benzene and naphthalene react with benzoyl peroxide (Lynch and Pausacker 1957*a*, 1957*b*). Levy and Szwarc (1954) have found that quinoline is 29 times more reactive than benzene towards attack, using acetyl peroxide and 63 times more reactive using propionyl peroxide (Smid and Szwarc 1956).

## IV. Acknowledgments

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# THE CHEMICAL CONSTITUENTS OF HIMANDTANRA SPECIES

## III. THE SYNTHESIS OF SOME HOMOLOGUES OF PYRENE

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*Summary*

In an attempt to identify a dehydrogenation product of himbacine, several pyrene homologues in which the alkyl groups are attached to the 1-, 2-, 6-, and 7-positions, have been synthesized. None of the synthetic substances was identical with the "natural" pyrene from himbacine and it is concluded that the latter, if a single substance, is probably substituted in two dissimilar rings.

### I. Introduction

The dehydrogenation of himbacine, or the substance obtained from it by reduction with lithium aluminium hydride, with selenium at 330–340 °C gave among other products, a hydrocarbon fraction which yielded a red crystalline 1,3,5-trinitrobenzene derivative. After repeated recrystallization this melted constantly and reasonably sharply at 183 °C and appeared to be a pure substance. Its analytical figures agreed best with $C_{19}H_{16}.C_6H_3O_6N_3$ but formulae with one more and with one less methylene group could not be completely excluded. Although obtained in a yield too small even to allow of the regeneration of the parent hydrocarbon, the substance represented the largest fragment of the alkaloid and its identification promised to provide valuable information on the structure of the latter (J. T. Pinhey, unpublished data).

The ultraviolet absorption spectrum of the hydrocarbon, calculated from that of its trinitrobenzene adduct, established that it was a pyrene derivative. However, it was not identical with any of the known alkyl pyrenes. The spectra of 1-, 3-, and 4-methyl-, 1,2-, 3,5-, 3,8-, 3,10-, and 4,9-dimethyl-, and 3,5,8-trimethylpyrenes have been recorded (Dannenberg and Brachert 1951; Friedel and Orchin 1951; De Clercq and Martin 1955) and although it was noted that the spectrum of the "natural" pyrene was rather similar to those of 3-methylpyrene and 1,2-dimethylpyrene, an unambiguous conclusion concerning the positions substituted in the pyrene nucleus could not be drawn.

It was therefore necessary to attempt to synthesize the "natural" pyrene. The small amount of data obtained from other work on himbacine indicated that one alkyl group was located at the 1-position and initially attention has been confined to pyrenes alkylated at one or more of the 1-, 2-, 6-, and 7-positions. By methods described below the following pyrenes were synthesized: 1-ethyl, 1-propyl, 1-*iso*propyl; 1-ethyl-2-methyl, 1,2-diethyl; 1,6-dimethyl, 1-ethyl-

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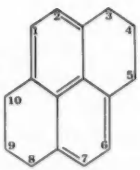
6-methyl, 1,6-diethyl; 1,7-dimethyl, 1,2,6-trimethyl, 1-ethyl-2,6-dimethyl; 1-ethyl-7-methyl, 1,7-diethyl, 1-ethyl-2,7-dimethyl, and 1,2-diethyl-6-methyl. Their ultraviolet spectra were measured (see below) and each was characterized by its trinitrobenzene derivative, but the " natural " pyrene trinitrobenzene derivative was not identical with any of them. The synthetic trinitrobenzene derivatives melted above 205 °C, with the exception of the 1-propyl- and 1-*iso*propylpyrene, and the 1,7-diethylpyrene adducts which had m.p. 176, 190, and 199 °C respectively. The mixed m.p. of the " natural " pyrene adduct with the adduct of 1-*iso*propylpyrene was depressed to 167–171 °C and with the adduct of 1,7-diethylpyrene was 189–190 °C. However, this cannot be regarded as good evidence for the identity of the " natural " pyrene with 1,7-diethylpyrene since it has been found that the melting points of trinitrobenzene adducts of alkyl pyrenes frequently show no depression on admixture. Also, on the spectroscopic evidence (see Section VI) 1,7-diethylpyrene may be excluded from consideration.

In view of the trends observed in the melting points of the synthetic adducts it seems safe to assume that the adducts of other members of the series that were not prepared would also have melting points above 205 °C. The conclusion is drawn that the " natural " adduct is either a mixture of difficultly separable substances or contains a pyrene substituted in dissimilar rings.

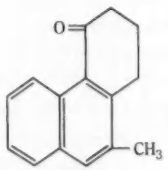
A convenient starting material for the synthesis of several of the required alkyl pyrenes appeared to be 3,4,5,8,9,10-hexahydropyrene (I) which had been shown by Vollmann *et al.* (1937) to yield mono- and diacetyl derivatives by the Friedel-Crafts reaction. They formulated the latter as a 1,6-derivative without offering direct proof. In fact, as shown below, it is the 1,7-derivative, but by choosing other reaction sequences, 1,6-disubstituted hexahydropyrenes may also be prepared.

## II. Monoalkyl Pyrenes

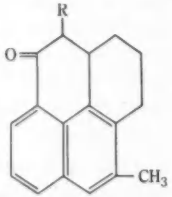
1-Acetylhexahydropyrene on Clemmensen reduction yielded 1-ethylhexahydropyrene, which gave 1-ethylpyrene by dehydrogenation with palladium-charcoal. This substance is described in Elsevier but not recorded elsewhere.



(I)



(II)



(III)

1-Propionylhexahydropyrene prepared from I and propionyl chloride was converted in a similar fashion to 1-propylpyrene. 1-*iso*Propylpyrene was obtained by dehydrogenating directly the crude carbinol resulting from the action of excess methylmagnesium iodide on 1-acetylhexahydropyrene.

## III. The 1,2-Series

Following the route used by Dannenberg and Brachert (1951) for the synthesis of 1,2-dimethylpyrene, 4-keto-1,2,3,4-tetrahydrophenanthrene was condensed with ethyl α-bromobutyrate by a Reformatsky reaction and the product dehydrated, reduced, and cyclized to 2-ethyl-1-keto-1,2,2a,3,4,5-hexahydropyrene. The ketone melted over a small range and probably consisted of two steroisomers of the same nature as those described by Dannenberg and Brachert in the case of the lower homologue. More obvious cases of this isomerism were encountered in several other ketones of this type during the course of the present work but no attempt was made to separate the isomers or pursue the matter further.

Clemmensen reduction of the ketone and dehydrogenation of the product yielded 1-ethylpyrene identical with the substance obtained in Section II. Reaction of the ketone with the appropriate Grignard reagent gave 1-ethyl-2-methyl- and 1,2-diethyl-2a,3,4,5-tetrahydropyrenes which were dehydrogenated to the corresponding pyrenes.

## IV. The 1,6-Series

### (*a*) *By Synthesis*

The Friedel-Crafts reaction of 6-methyltetralin (Fieser and Jones 1938) with succinic anhydride gave the 7-keto acid, the structure of which followed from its oxidation by hypochlorite to 6-methyltetralin-7-carboxylic acid, identical with the acid obtained by a similar oxidation of 7-acetyl-6-methyltetralin of known constitution (Karrer and Epprecht 1940). Also, both samples yielded the same 2-methylnaphthalene-3-carboxylic acid on dehydrogenation.

Clemmensen reduction of the keto acid followed by dehydrogenation furnished γ-2-(3-methylnaphthyl)butyric acid which was cyclized through its acid chloride to 4-keto-10-methyl-1,2,3,4-tetrahydrophenanthrene (II). As a further check on its identity, the ketone (II) was reduced and dehydrogenated to the known 9-methylphenanthrene.

Through the usual steps involving a Reformatsky reaction with iodoacetic ester, dehydration, reduction, and cyclization the ketone (II) was converted to 1-keto-6-methyl-1,2,2*a*,3,4,5-hexahydropyrene (III; R=H). By reduction and dehydrogenation this afforded the known 1-methylpyrene and by reaction with the appropriate Grignard reagent followed by dehydrogenation, 1,6-dimethyl- and 1-ethyl-6-methylpyrenes.

### (*b*) *From Hexahydropyrene*

1-Ethylhexahydropyrene prepared from hexahydropyrene, as in Section II, gave 6-acetyl-1-ethylhexahydropyrene on treatment with acetyl chloride and aluminium chloride. Oxidation of the ketone by the iodine-pyridine method of King (1944) afforded 1-ethylhexahydropyrene-6-carboxylic acid, the methyl ester of which was reduced by lithium aluminium hydride to the corresponding carbinol. Dehydrogenation with palladium-charcoal then yielded 1-ethyl-6-methylpyrene identical with the substance prepared as above.

Reduction of 6-acetyl-1-ethylhexahydropyrene by the Clemmensen procedure yielded 1,6-diethylhexahydropyrene which was dehydrogenated to 1,6-diethylpyrene. This substance was also prepared by another route. Bromination of 1-ethylhexahydropyrene afforded the 6-bromo-derivative which by successive treatment with butyl lithium and ethyl iodide gave 1,6-diethylhexahydropyrene and thence 1,6-diethylpyrene.

## V. The 1,7-Series

### (*a*) *By Synthesis*

The ketone (II) was reacted with ethyl α-iodopropionate and the product converted as usual to 1-keto-2,6-dimethyl-1,2,2a,3,4,5-hexahydropyrene (III; R=$CH_3$), which by reduction with lithium aluminium hydride and dehydrogenation yielded 1,7-dimethylpyrene. By reaction with methyl and ethyl magnesium iodide followed by dehydrogenation, the ketone (III; R=$CH_3$) afforded 1,2,6-trimethyl- and 1-ethyl-2,6-dimethylpyrenes respectively.

By a similar series of reactions the ketone (III; R=$C_2H_5$) was prepared from II and ethyl α-iodobutyrate and converted to 1-ethyl-7-methyl-, 1-ethyl-2,7-dimethyl-, and 1,2-diethyl-6-methylpyrenes.

### (*b*) *From Hexahydropyrene*

Following the methods of Vollmann *et al.* (1937), hexahydropyrene was acylated to 1,7-diacetylhexahydropyrene which was oxidized to hexahydropyrene-1,7-dicarboxylic acid. The dimethyl ester on reduction with lithium aluminium hydride gave the corresponding bishydroxymethyl derivative which on dehydrogenation yielded 1,7-dimethylpyrene identical with the substance prepared as above.

1,7-Diethylpyrene was readily secured by the dehydrogenation of 1,7-diethylhexahydropyrene, obtained by Clemmensen reduction of the diacetyl derivative.

The diacetyl derivative on partial oxidation by the iodine-pyridine method afforded 1-acetylhexahydropyrene-7-carboxylic acid. The methyl ester was reduced successively by the Clemmensen procedure and lithium aluminium hydride to 1-ethyl-7-hydroxymethylhexahydropyrene which on dehydrogenation gave 1-ethyl-7-methylpyrene identical with the product prepared as above.

## VI. Ultraviolet Spectra

Spectroscopic data for the synthetic pyrenes, determined in ethanol on a Warren Spectracord, Model 4000, are collected in Table 1 which also includes pyrene, 1-methylpyrene, 4,9-dimethylpyrene (Friedel and Orchin 1951), 1,2-dimethylpyrene (Dannenberg and Brachert 1951), 3,5-, 3,8-, and 3,10-dimethylpyrenes, 3,5,8-trimethylpyrene, and 4-methylpyrene (De Clercq and Martin 1955).

The introduction of a methyl group in the pyrene nucleus shifts the absorption maxima to longer wavelengths, particularly in the region above 300 mμ, the greatest effect being produced by methylation at the 3-position. When a second methyl group is present at the 5-, 8-, or 10-position, each of which corresponds structurally with the 3-position, a further, almost equal, shift occurs.

TABLE 1

ULTRAVIOLET ABSORPTION DATA FOR PYRENE DERIVATIVES IN ETHANOL

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Pyrene | | | | | | | | | |
| $\lambda_{max.}$ (mμ) | 232 | 241 | 253* | 262 | 272 | 295* | 306 | 318 | 334 |
| log ε | 4·65 | 4·94 | 4·07 | 4·42 | 4·70 | 3·66 | 4·06 | 4·49 | 4·68 |
| 1-Methyl- | | | | | | | | | |
| $\lambda_{max.}$ (mμ) | 233 | 242 | 254* | 264 | 274 | 297* | 307 | 321 | 336 |
| log ε | 4·65 | 4·86 | 4·18 | 4·44 | 4·65 | 3·72 | 4·10 | 4·45 | 4·64 |
| 1-Ethyl- | | | | | | | | | |
| $\lambda_{max.}$ (mμ) | 233 | 241·5 | 253* | 263·5 | 274·5 | 296·5* | 307·5 | 321·5 | 336 |
| log ε | 4·61 | 4·86 | 4·04 | 4·38 | 4·66 | 3·69 | 4·04 | 4·43 | 4·61 |
| 1-Propyl- | | | | | | | | | |
| $\lambda_{max.}$ (mμ) | 232·5 | 241·5 | 254* | 264 | 274 | 296* | 308 | 322 | 337 |
| log ε | 4·59 | 4·79 | 4·03 | 4·38 | 4·63 | 3·62 | 4·03 | 4·42 | 4·59 |
| 1-*iso*Propyl- | | | | | | | | | |
| $\lambda_{max.}$ (mμ) | 232·5 | 241·5 | 254* | 263·5 | 274 | 296* | 307 | 321 | 336 |
| log ε | 4·60 | 4·84 | 4·03 | 4·37 | 4·58 | 3·61 | 4·02 | 4·40 | 4·54 |
| 1,2-Dimethyl- | | | | | | | | | |
| $\lambda_{max.}$ (mμ) | 235·5 | 244 | 257 | 267 | 277·5 | 299 | 312·5 | 324·5 | 340 |
| log ε | 4·56 | 4·76 | 4·08 | 4·38 | 4·60 | 3·70 | 4·02 | 4·31 | 4·47 |
| 1-Ethyl-2-methyl- | | | | | | | | | |
| $\lambda_{max.}$ (mμ) | 234·5 | 243 | 257* | 266 | 277 | 297* | 311 | 325 | 340 |
| log ε | 4·64 | 4·78 | 4·01 | 4·37 | 4·62 | 3·56 | 4·01 | 4·39 | 4·56 |
| 1,2-Diethyl- | | | | | | | | | |
| $\lambda_{max.}$ (mμ) | 234·5 | 243 | 259* | 266 | 277 | 297* | 312 | 325 | 340 |
| log ε | 4·58 | 4·80 | 4·03 | 4·39 | 4·64 | 3·59 | 4·03 | 4·41 | 4·59 |
| 1,6-Dimethyl- | | | | | | | | | |
| $\lambda_{max.}$ (mμ) | 234 | 243 | 255* | 265 | 276 | 297* | 308 | 323 | 337 |
| log ε | 4·59 | 4·83 | 4·05 | 4·41 | 4·68 | 3·57 | 4·02 | 4·43 | 4·63 |
| 1-Ethyl-6-methyl- | | | | | | | | | |
| $\lambda_{max.}$ (mμ) | 234 | 243 | 255* | 265 | 276 | 297* | 308 | 323 | 337 |
| log ε | 4·59 | 4·84 | 4·02 | 4·40 | 4·69 | 3·59 | 4·01 | 4·42 | 4·61 |
| 1,6-Diethyl- | | | | | | | | | |
| $\lambda_{max.}$ (mμ) | 234 | 243 | 255* | 265 | 276 | 297* | 308 | 323 | 338 |
| log ε | 4·57 | 4·81 | 4·01 | 4·40 | 4·68 | 3·59 | 3·99 | 4·40 | 4·57 |
| 1,7-Dimethyl- | | | | | | | | | |
| $\lambda_{max.}$ (mμ) | 234 | 242·5 | 255* | 265 | 276 | 296* | 308 | 322 | 337 |
| log ε | 4·56 | 4·77 | 4·03 | 4·34 | 4·60 | 3·61 | 4·02 | 4·41 | 4·60 |
| 1-Ethyl-7-methyl- | | | | | | | | | |
| $\lambda_{max.}$ (mμ) | 234·5 | 243 | 255* | 265 | 276·5 | 296* | 309 | 323 | 338 |
| log ε | 4·57 | 4·79 | 4·07 | 4·36 | 4·59 | 3·65 | 4·03 | 4·40 | 4·57 |
| 1,7-Diethyl- | | | | | | | | | |
| $\lambda_{max.}$ (mμ) | 234·5 | 243 | 255* | 265·5 | 276·5 | 296* | 309 | 323 | 338 |
| log ε | 4·56 | 4·77 | 4·01 | 4·35 | 4·59 | 3·62 | 4·01 | 4·39 | 4·55 |
| 1,2,6-Trimethyl- | | | | | | | | | |
| $\lambda_{max.}$ (mμ) | 236 | 245 | 257* | 267 | 278·5 | 302* | 311 | 325 | 340 |
| log ε | 4·58 | 4·80 | 4·05 | 4·40 | 4·67 | 3·63 | 4·02 | 4·40 | 4·56 |
| 1,2-Diethyl-6-methyl- | | | | | | | | | |
| $\lambda_{max.}$ (mμ) | 235·5 | 244·5 | 257* | 267·5 | 279 | 299* | 313 | 326 | 342 |
| log ε | 4·57 | 4·82 | 4·07 | 4·42 | 4·69 | 3·56 | 3·94 | 4·42 | 4·60 |

* These values may not be accurate since the peaks in these regions are rather broad.

TABLE 1 (*Continued*)

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 1-Ethyl-2,7-dimethyl- | | | | | | | | | |
| $\lambda_{max.}$ (mμ) .. | 235·5 | 244·5 | 258* | 267·5 | 278·5 | 299* | 313 | 326 | 342 |
| log ε .. .. | 4·57 | 4·83 | 4·05 | 4·41 | 4·68 | 3·55 | 4·03 | 4·41 | 4·57 |
| 1-Ethyl-2,6-dimethyl- | | | | | | | | | |
| $\lambda_{max.}$ (mμ) .. | 235·5 | 244·5 | 258* | 267 | 278·5 | 302* | 312 | 326 | 341 |
| log ε .. .. | 4·58 | 4·79 | 4·07 | 4·41 | 4·67 | 3·67 | 4·05 | 4·42 | 4·58 |
| 3-Methyl- | | | | | | | | | |
| $\lambda_{max.}$ (mμ) .. | 233·5 | 242 | 255 | 265 | 275·5 | | 312·5 | 326 | 342·5 |
| log ε .. .. | 4·62 | 4·88 | 4·02 | 4·39 | 4·71 | | 4·05 | 4·43 | 4·61 |
| 3,5-Dimethyl- | | | | | | | | | |
| $\lambda_{max.}$ (mμ) .. | 235 | 243 | 257·5 | 267 | 278 | | 318·5 | 332·5 | 349 |
| log ε .. .. | 4·61 | 4·84 | 4·04 | 4·43 | 4·74 | | 4·07 | 4·44 | 4·59 |
| 3,8-Dimethyl- | | | | | | | | | |
| $\lambda_{max.}$ (mμ) .. | 235 | 244 | 257 | 267 | 278 | | 318 | 331 | 348 |
| log ε .. .. | 4·64 | 4·89 | 4·02 | 4·46 | 4·80 | | 4·12 | 4·51 | 4·71 |
| 3,10-Dimethyl- | | | | | | | | | |
| $\lambda_{max.}$ (mμ) .. | 235 | 244 | 257 | 267 | 278 | | 318 | 333 | 349 |
| log ε .. .. | 4·67 | 4·89 | 4·11 | 4·47 | 4·80 | | 4·11 | 4·47 | 4·64 |
| 3,5,8-Trimethyl- | | | | | | | | | |
| $\lambda_{max.}$ (mμ) .. | 237 | 245 | 260 | 270 | 281 | | 323 | 338 | 356 |
| log ε .. .. | 4·75 | 4·96 | 4·11 | 4·56 | 4·92 | | 4·23 | 4·61 | 4·78 |
| 4-Methyl- | | | | | | | | | |
| $\lambda_{max.}$ (mμ) .. | 235 | 244 | 254 | 264 | 276 | | 307 | 321 | 337 |
| log ε .. .. | 4·72 | 4·98 | 4·34 | 4·49 | 4·69 | | 4·11 | 4·47 | 4·69 |
| 4,9-Dimethyl- | | | | | | | | | |
| $\lambda_{max.}$ (mμ) .. | 236 | 246 | 254* | 265 | 276·5 | 297* | 308 | 322 | 338 |
| log ε .. .. | 4·75 | 5·0 | 4·29 | 4·50 | 4·70 | 3·74 | 4·13 | 4·50 | 4·72 |
| " Natural " | | | | | | | | | |
| $\lambda_{max.}$ (mμ) .. | 236·5 | 245 | 255·5* | 267 | 278 | 301* | 315 | 327·5 | 342·5 |
| log ε .. .. | 4·63 | 4·82 | 4·12 | 4·38 | 4·62 | 3·72 | 4·04 | 4·39 | 4·55 |

* These values may not be accurate since the peaks in these regions are rather broad.

In the one example where a third methyl group is present in a position of this type, that is, 3,5,8-trimethylpyrene, yet another large shift is apparent.

A 4-methyl group has considerably less influence than a 3-methyl group and there is scarcely any further shift of the maxima when a second methyl group is also present at the other structurally equivalent, that is, 9-position.

The effect of a 1-methyl group is about the same as that of a 4-methyl group. A second methyl group at the 2-position causes a further shift so that the spectrum then approximates that of 3-methylpyrene. On the other hand, alkylation at the 6- or 7-position has only a very slight effect on the spectrum of either 1-alkyl or 1,2-dialkyl pyrene.

The spectrum of the natural pyrene shows some resemblance to the spectra of 3-methyl-, 1,2-dialkyl, and 1,2,6-trialkyl pyrenes, but obviously differs at several points, in particular by having a rather flat maximum in the region of 315 mμ. These differences may be due to the presence of a persistent impurity or they may perhaps be due to alkylation of the pyrene nucleus in two dissimilar rings.

## VII. Experimental

Melting points are uncorrected. Light petroleum refers to the fraction of b.p. 60–90 °C. Analyses are by Miss B. Stevenson.

### (*a*) *Monoalkyl Pyrenes*

(i) *1-Ethylhexahydropyrene.*—A mixture of 1-acetylhexahydropyrene (12·5 g), amalgamated zinc (30 g), concentrated hydrochloric acid (60 ml), water (25 ml), and toluene (25 ml) was refluxed for 30 hr, additional hydrochloric acid (10 ml) being added every 8 hr. The toluene layer was evaporated and a solution of the residue in light petroleum passed through a column of alumina. The product (75% yield) crystallized from ethanol in colourless needles, m.p. 61–62 °C (Found: C, 91·2; H, 8·6%. Calc. for $C_{18}H_{20}$: C, 91·5; H, 8·5%).

(ii) *1-Ethylpyrene.*—Ethylhexahydropyrene (0·5 g) and 10% palladium-charcoal (0·2 g) were heated at 300 °C for 1 hr, cooled, and extracted with light petroleum. The extract was passed through a column of alumina and the colourless eluates evaporated to dryness. The residue crystallized from ethanol in colourless needles (0·4 g), m.p. 75 °C (lit. 75 °C). The trinitrobenzene adduct formed orange needles from benzene-ethanol, m.p. 209 °C (lit. 209–210 °C).

(iii) *1-Propionylhexahydropyrene.*—Hexahydropyrene (4·2 g), propionyl chloride (2·2 g), anhydrous aluminium chloride (3·2 g), and dry benzene (60 ml) were stirred and refluxed for 3 hr. After cooling, the mixture was decomposed with cold dilute acid and the organic layer separated and evaporated. The residue crystallized from ethanol as colourless needles (4·4 g), m.p. 89 °C (Found: C, 86·0; H, 7·6%. Calc. for $C_{19}H_{22}O$: C, 86·3; H, 7·6%).

(iv) *1-Propylhexahydropyrene.*—Reduction as in (i) above and crystallization from ethanol gave colourless needles (85% yield), m.p. 78 °C (Found: C, 91·0; H, 9·0%. Calc. for $C_{19}H_{22}$: C, 91·1; H, 8·9%).

(v) *1-Propylpyrene.*—Dehydrogenation and purification as in (ii) above, followed by crystallization from ethanol gave colourless needles (80% yield), m.p. 49–50 °C (Found: C, 93·2; H, 6·6%. Calc. for $C_{19}H_{16}$: C, 93·4; H, 6·6%).

The trinitrobenzene adduct crystallized from benzene-ethanol as orange needles, m.p. 176 °C (Found: C, 65·3; H, 4·0%. Calc. for $C_{25}H_{19}O_6N_3$: C, 65·6; H, 4·2%).

The picrate formed deep red needles from ethanol, m.p. 156 °C (Found: C, 63·1; H, 4·0%. Calc. for $C_{25}H_{19}O_7N_3$: C, 63·4; H, 4·1%).

(vi) *1-iso-Propylpyrene.*—Acetylhexahydropyrene (2·0 g) in ether (75 ml) was added with stirring to an ice-cold solution of methylmagnesium iodide prepared from methyl iodide (6·2 g), magnesium (1·0 g), and ether (75 ml), when an insoluble complex separated almost immediately. After stirring for a further 2 hr, the mixture was kept overnight and decomposed with cold dilute acid. The organic layer was separated, washed, dried, and evaporated. The residue was treated in the normal manner with Girard's Reagent P and the non-ketonic portion heated with 10% palladium-charcoal (0·7 g) at 300 °C for 1 hr. Working up in the usual manner and crystallization from ethanol gave colourless prisms (1·1 g), m.p. 69–70 °C (Found: C, 93·2; H, 6·6%. Calc. for $C_{19}H_{16}$: C, 93·4; H, 6·6%).

The trinitrobenzene adduct separated from benzene-ethanol as orange needles, m.p. 190 °C (Found: C, 65·5; H, 4·3%. Calc. for $C_{25}H_{19}O_6N_3$: C, 65·6; H, 4·2%).

The picrate crystallized from ethanol in deep red needles, m.p. 171 °C (Found: C, 63·2; H, 4·2%. Calc. for $C_{25}H_{19}O_7N_3$: C, 63·4; H, 4·1%).

### (*b*) *The 1,2-Series*

(i) *α,4-(1,2,3,4-Tetrahydrophenanthryl)butyric Acid.*—When a mixture of 4-keto-1,2,3,4-tetrahydrophenanthrene (5·0 g), benzene (70 ml), ether (60 ml), zinc filings (6·0 g), ethyl α-bromobutyrate (5·0 ml), and iodine (0·2 g) was stirred and heated under reflux, a reaction commenced almost immediately. After 1·5 hr, more zinc (5·0 g) and ethyl α-bromobutyrate (5·0 ml) were added and heating continued for a further 4·5 hr. The mixture was decomposed with cold dilute

acid, the organic layer separated, washed thoroughly, and dried. The solvent and excess ester were removed under reduced pressure but the residue could not be obtained crystalline even after treatment with Girard's Reagent P which removed only a trace of ketonic material.

The oily product (6·5 g), benzene (65 ml), pyridine (6·5 ml), and phosphorus oxychloride (15 g) were refluxed for 0·5 hr. After cooling, the mixture was poured into cold dilute acid, the organic layer separated, washed thoroughly, and dried. Removal of the solvent gave a gum which could not be obtained crystalline. However, hydrolysis of a small portion of either it or the initial Reformatsky reaction product (0·2 g) with potassium hydroxide (0·25 g) in butanol (5 ml) for 3 hr gave α,4-(1,2,3,4-tetrahydrophenanthrylidene)butyric acid which crystallized from aqueous ethanol in colourless needles, m.p. 177 °C (decomp.) (Found: C, 80·9; H, 6·7%. Calc. for $C_{18}H_{18}O_2$: C, 81·2; H, 6·8%).

The unsaturated ester in ethanol (200 ml) was hydrogenated at room temperature and pressure in the presence of platinum oxide, when uptake of hydrogen was complete in about 5 hr. After filtering, the solvent was removed and the residue hydrolysed by refluxing for 3 hr with potassium hydroxide (6·5 g) in butanol (80 ml). The crude acid, isolated in the usual manner, formed shining colourless plates (4·0 g), m.p. 182 °C, on crystallization from aqueous ethanol (Found: C, 80·5; H, 7·7%. Calc. for $C_{18}H_{20}O_2$: C, 80·6; H, 7·5%).

(ii) *2-Ethyl-1-keto-1,2,2a,3,4,5-hexahydropyrene.*—A solution of the acid (5·4 g) and purified thionyl chloride (5 ml) in benzene (60 ml) was refluxed for 1 hr. After removing solvent and excess reagent under reduced pressure, the residue was dissolved in benzene (60 ml), the solution cooled in ice, and treated with a solution of stannic chloride (14 g) in benzene (20 ml) during 0·25 hr, with stirring. After a further 0·5 hr, the reaction mixture was decomposed with cold dilute acid, the organic layer separated, washed, and dried. Removal of the solvent gave a crystalline residue, which recrystallized from methanol in pale yellow plates (4·0 g), m.p. 126–129 °C (Found: C, 86·2; H, 7·2. Calc. for $C_{18}H_{18}O$: C, 86·4; H, 7·3%).

(iii) *1,2-Diethyl-2a,3,4,5-tetrahydropyrene.*—A suspension of the ketone (2·0 g) in ether (50 ml) was added with stirring to ethereal ethylmagnesium iodide prepared from ethyl iodide (6·6 g), magnesium (1·0 g), and ether (75 ml). After keeping overnight, the reaction mixture was worked up as usual and the crude product purified by passing a solution of it in light petroleum through a column of alumina. The pure hydrocarbon (1·6 g) crystallized from ethanol in colourless needles, m.p. 110 °C (Found: C, 91·6; H, 8·5%. Calc. for $C_{20}H_{22}$: C, 91·6; H, 8·4%).

(iv) *1,2-Diethylpyrene.*—Dehydrogenation of the tetrahydro compound and purification as usual, followed by recrystallization from ethanol gave shining colourless plates, m.p. 100 °C (80% yield) (Found: C, 92·7; H, 7·0%. Calc. for $C_{20}H_{18}$: C, 93·0; H, 7·0%).

The trinitrobenzene adduct, red needles from benzene-ethanol, had m.p. 207 °C (Found: C, 65·9; H, 4·5%. Calc. for $C_{26}H_{21}O_6N_3$: C, 66·2; H, 4·5%).

The picrate crystallized from ethanol as deep red needles, m.p. 182 °C (Found: C, 64·1; H, 4·5%. Calc. for $C_{26}H_{21}O_7N_3$: C, 64·1; H, 4·3%).

(v) *1-Methyl-2-ethyl-2a,3,4,5-tetrahydropyrene.*—The substance prepared as in (iii) above but using methylmagnesium iodide, was obtained as pale yellow, light-sensitive needles, m.p. 109 °C, from ethanol (yield 65%) (Found: C, 91·5; H, 8·3%. Calc. for $C_{19}H_{20}$: C, 91·9; H, 8·1%).

(vi) *1-Ethyl-2-methylpyrene.*—Dehydrogenation as usual gave colourless plates (75% yield) from ethanol, m.p. 101 °C (Found: C, 93·3; H, 6·5%. Calc. for $C_{19}H_{16}$: C, 93·4; H, 6·6%).

The trinitrobenzene derivative separated from benzene-ethanol in deep red needles, m.p. 236 °C (Found: C, 65·8; H, 4·3%. Calc. for $C_{25}H_{19}O_6N_3$: C, 65·6; H, 4·2%).

The picrate was obtained as deep red needles from ethanol, m.p. 217 °C (Found: C, 63·4; H, 4·1%. Calc. for $C_{25}H_{19}O_7N_3$: C, 63·4; H, 4·1%).

(vii) *1-Ethylpyrene.*—Clemmensen reduction of the ketone of (ii) above, followed by dehydrogenation in the usual manner gave 1-ethylpyrene (60% yield), m.p. and mixed m.p. 75 °C. The trinitrobenzene adduct had m.p. and mixed m.p. 209 °C.

*(c) The 1,6-Series*

(i) β,7-*(6-Methyl-1,2,3,4-tetrahydronaphthoyl)propionic Acid.*—Powdered aluminium chloride (175 g) was added during 0·25 hr to a vigorously stirred mixture of powdered succinic anhydride (100 g) 6-methyltetralin (146 g) and benzene (800 ml) at room temperature. After a further hour at room temperature, the mixture was stirred and refluxed for 4 hr, then cooled and treated with cold dilute acid. The benzene layer was separated, washed thoroughly with water, and then extracted repeatedly with dilute sodium carbonate. The combined extracts were acidified and extracted with ether. The ethereal extract, after washing and drying, was treated with excess ethereal diazomethane. The methyl ether was isolated by distillation as a pale yellow viscous oil (65% yield), b.p. 146–152 °C/0·2 mm. The analytical sample was a pale yellow viscous oil, b.p. 148–150 °C/0·2 mm, $n_D^{22}$ 1·5422 (Found: C, 73·6; H, 7·6. Calc. for $C_{16}H_{20}O_3$: C, 73·8; H, 7·7%).

Saponification of the ester yielded the acid which crystallized from light petroleum in colourless needles, m.p. 105 °C, after softening at about 99 °C (Found: C, 73·0; H, 7·4%. Calc. for $C_{15}H_{18}O_3$: C, 73·1; H, 7·4%).

(ii) *6-Methyltetralin-7-carboxylic Acid.*—(1) Chlorine was passed into an ice-cold solution of sodium hydroxide (18·4 g) in water (150 ml) until it was neutral to litmus. More sodium hydroxide (3·4 g) in water (10 ml) was added, followed by 6-acetyl-7-methyltetralin (9·3 g). The mixture was stirred vigorously and warmed to 85 °C when a brisk reaction ensued and the temperature rose to 105 °C. Stirring was continued until the temperature fell to 60 °C, when excess hypochlorite was destroyed by the addition of sodium bisulphite. Acidification gave an acid (8·0 g) which was purified by dissolution in dilute sodium carbonate and regeneration, recrystallization from light petroleum, and sublimation at 130 °C/0·2 mm. It formed colourless needles, m.p. 173 °C, on slow heating, and m.p. 178 °C, after softening at about 173 °C on rapid heating (Found: C, 75·7; H, 7·4%. Calc. for $C_{12}H_{14}O_2$: C, 75·8; H, 7·4%).

The methyl ester prepared by the use of diazomethane was a colourless mobile oil, b.p. 98–99 °C/0·2 mm, $n_D^{22}$ 1·5432 (Found: C, 76·6; H, 7·8%. Calc. for $C_{13}H_{16}O_2$: C, 76·4; H, 7·9%).

(2) By the same procedure the acid (9·0 g) prepared in (i) above was oxidized to an acid (5·2 g) which had m.p. and mixed m.p. 173 °C (Found: C, 76·0; H, 7·5%. Calc. for $C_{12}H_{14}O_2$: C, 75·8; H, 7·4%), and which was converted to its methyl ester, b.p. 98–99 °C/0·2 mm, $n_D^{22}$ 1·5431.

(iii) *2-Methylnaphthalene-3-carboxylic Acid.*—Each of the above esters (4 g) was heated with 20% palladium-charcoal (0·1 g) at 275–300 °C for 6 hr. Hydrolysis of the reaction product yielded an acid (2·1 g) which crystallized from benzene in colourless needles, m.p. and mixed m.p. 199 °C (Found: C, 77·3; H, 5·3%. Calc. for $C_{12}H_{10}O_2$: C, 77·4; H, 5·4%).

(iv) *Methyl-γ,7-(6-methyl-1,2,3,4-tetrahydronaphthyl)butyric Acid.*—The keto-ester (150 g), prepared in (i) above, amalgamated zinc (300 g), concentrated hydrochloric acid (600 ml), water (250 ml), and toluene (300 ml) were refluxed for 48 hr, additional hydrochloric acid (90 ml) being added at 8 hourly intervals. The organic layer was separated, washed with water, dried, and the toluene removed. The residue was treated with excess ethereal diazomethane and the product isolated by distillation. It formed a colourless oil (128 g), b.p. 124–126 °C/0·2 mm, $n_D^{21}$ 1·5270 (Found: C, 77·8; H, 8·9%. Calc. for $C_{16}H_{22}O_2$: C, 78·0; H, 9·0%).

(v) *γ,2(3-Methylnaphthyl)butyric Acid.*—The above ester (125 g) and 20% palladium-charcoal (3·0 g) were heated in a metal bath at 275–320 °C for 6 hr under reflux. After cooling the reaction mixture was extracted with ether and the extract treated with excess ethereal diazomethane. Distillation yielded the product as a colourless viscous oil (105 g), b.p. 131–133 °C/0·2 mm, $n_D^{20}$ 1·5760 (Found: C, 79·4; H, 7·6%. Calc. for $C_{15}H_{18}O_2$: C, 79·3; H, 7·5%).

Saponification of the ester (104 g) with potassium hydroxide (100 g) in butanol (750 ml) for 3 hr gave the acid (80 g) which crystallized from light petroleum in colourless needles, m.p. 110–112 °C (Found: C, 79·0; H, 7·2%. Calc. for $C_{15}H_{16}O_2$: C, 78·9; H, 7·1%).

(vi) *4-Keto-10-methyl-1,2,3,4-tetrahydrophenanthrene.*—The above acid (40 g) and thionyl chloride (50 ml) in benzene (350 ml) were refluxed for 2 hr and then the solvent and excess reagent were removed under reduced pressure. A solution of the residue in benzene (350 ml) was stirred and cooled to 0 °C whilst a solution of stannic chloride (40 ml) in benzene (50 ml) was added during 0·5 hr. After a further 0·5 hr the reaction mixture was treated with cold dilute acid and the benzene layer separated, washed thoroughly, and dried. The ketone obtained by distillation was a pale yellow viscous oil, b.p. 150–154 °C/0·5 mm, which crystallized on keeping. Recrystallization from methanol gave colourless prisms (31·8 g), m.p. 86–87 °C (Found : C, 85·7 ; H, 6·7%. Calc. for $C_{15}H_{14}O$ : C, 85·7 ; H, 6·7%).

(vii) *9-Methylphenanthrene.*—Clemmensen reduction of the above ketone by the usual procedure gave 10-methyl-1,2,3,4-tetrahydrophenanthrene (85% yield) as an oil which yielded a picrate crystallizing from ethanol in orange needles, m.p. 144 °C (Found : C, 59·3 ; H, 4·6%. Calc. for $C_{21}H_{19}O_7N_3$ : C, 59·3 ; H, 4·5%).

Decomposition of the picrate, followed by dehydrogenation in the usual manner, gave 9-methylphenanthrene, m.p. 91 °C (lit. 91 °C), characterized by its picrate, m.p. 152 °C (lit. 153 °C).

(viii) *4-(10-Methyl-1,2,3,4-tetrahydrophenanthrylidene)acetic Acid.*—The ketone II (5·3 g) in ether (75 ml) and benzene (75 ml) was reacted with ethyl iodoacetate (5 ml) and zinc filings (10 g) and the product isolated after treatment with Girard's Reagent P, in the usual manner. The oily ester was dehydrated with phosphorus oxychloride and the resulting unsaturated ester saponified with potassium hydroxide in butanol to yield the required acid which crystallized from methanol in colourless prisms (4·0 g), m.p. 223 °C (decomp.) (Found : C, 80·8 ; H, 6·4%. Calc. for $C_{17}H_{16}O_2$ : C, 80·9 ; H, 6·4%).

(ix) *4-(10-Methyl-1,2,3,4-tetrahydrophenanthryl)acetic Acid.*—Catalytic hydrogenation of the above acid by the usual procedure gave the saturated acid which separated from methanol in colourless prisms, m.p. 168 °C (Found : C, 80·2 ; H, 7·3%. Calc. for $C_{17}H_{18}O_2$ : C, 80·3 ; H, 7·1%).

(x) *1-Keto-6-methyl-1,2,2a,3,4,5-hexahydropyrene.*—The acid was converted to the acid chloride with thionyl chloride and cyclized by stannic chloride to the ketone III (R=H) which formed colourless needles from ethanol (80% yield), m.p. 172 °C (Found : C, 86·1 ; H, 6·8%. Calc. for $C_{17}H_{16}O$ : C, 86·4 ; H, 6·8%).

(xi) *1-Methylpyrene.*—The above ketone was reduced by amalgamated zinc and hydrochloric acid and the product dehydrogenated as usual to 1-methylpyrene, m.p. 148 °C (lit. 149 °C), which formed a trinitrobenzene adduct, m.p. 253–254 °C (lit. 253–254 °C).

(xii) *1,6-Dimethylpyrene.*—Reaction of the ketone III (R=H) with methylmagnesium iodide and dehydrogenation of the product gave the hydrocarbon which separated from benzene-ethanol in pale yellow plates, m.p. 190–192 °C (Found : C, 93·5 ; H, 6·0%. Calc. for $C_{18}H_{14}$ : C, 93·9 ; H, 6·1%).

The trinitrobenzene adduct, orange needles from benzene-ethanol had m.p. 256 °C (Found : C, 64·8 ; H, 3·8%. Calc. for $C_{24}H_{17}O_6N_3$ : C, 65·0 ; H, 3·9%).

The picrate crystallized from ethanol in red needles, m.p. 234 °C (decomp.) (Found : C, 62·5 ; H, 3·7%. Calc. for $C_{24}H_{17}O_7N_3$ : C, 62·7 ; H, 3·7%).

(xiii) *1-Ethyl-6-methylpyrene.*—The substance crystallized from benzene-ethanol in very pale yellow needles, m.p. 145 °C (Found : C, 93·3 ; H, 6·6%. Calc. for $C_{19}H_{16}$ : C, 93·4 ; H, 6·6%).

The trinitrobenzene adduct formed orange needles from benzene-ethanol, m.p. 220 °C (Found : C, 65·4 ; H, 4·0%. Calc. for $C_{25}H_{19}O_6N_3$ : C, 65·6 ; H, 4·2%).

The 2,4,7-trinitrofluorenone complex separated from acetic acid as red-brown needles, m.p. 189 °C (decomp.) (Found : C, 68·3 ; H, 3·9%. Calc. for $C_{32}H_{21}O_7N_3$ : C, 68·7 ; H, 3·8%).

(xiv) *6-Acetyl-1-ethylhexahydropyrene.*—A mixture of acetyl chloride (4·0 g), 1-ethylhexahydropyrene (10·0 g), aluminium chloride (7·0 g), and benzene (200 ml) was stirred and refluxed for 4 hr. Working up in the usual manner gave a product which crystallized from ethanol in cream

coloured needles (7·2 g), m.p. 145 °C (Found : C, 86·5 ; H, 8·0%. Calc. for $C_{20}H_{22}O$ : C, 86·3 ; H, 8·0%).

The 2,4-dinitrophenylhydrazone formed red needles, m.p. 194 °C, from ethanol-chloroform (Found : C, 67·8 ; H, 5·8%. Calc. for $C_{32}H_{26}O_4N_4$ : C, 68·1 ; H, 5·7%).

(xv) *1-Ethylhexahydropyrene-6-carboxylic Acid.*—A mixture of the above ketone (7·0 g), iodine (6·2 g), and pyridine (20 ml) was heated on the water-bath with frequent shaking for 1·5 hr. After keeping overnight at room temperature excess pyridine was removed under reduced pressure and the residue triturated with boiling benzene (4 × 50 ml). From these extracts, starting material (1·2 g) was recovered.

The benzene-insoluble residue was triturated with cold water (3 × 30 ml) and the remaining material heated on the water-bath with water (150 ml) containing sodium hydroxide (5 g) for 1·5 hr. After cooling, the mixture was acidified and the crude acid collected. By treatment with excess ethereal diazomethane the acid was converted to its methyl ester which after chromatography on alumina in benzene-light petroleum, separated from methanol in colourless needles (4·3 g), m.p. 93 °C (Found : C, 81·4 ; H, 7·3%. Calc. for $C_{20}H_{22}O_2$ : C, 81·6 ; H, 7·5%).

Hydrolysis of a small portion of the ester with potassium hydroxide in butanol gave the acid which crystallized from ethanol in colourless needles, m.p. 257 °C (Found : C, 81·1 ; H, 7·1%. Calc. for $C_{19}H_{20}O_2$ : C, 81·4 ; H, 7·2%).

(xvi) *1-Ethyl-6-hydroxymethylhexahydropyrene.*—The ester (4·0 g) was reduced with lithium aluminium hydride (0·55 g) and ether (250 ml) by using the Soxhlet technique. The product, isolated in the normal manner, crystallized from ethanol in colourless feathery needles (2·9 g), m.p. 170 °C (Found : C, 85·5 ; H, 8·5%. Calc. for $C_{19}H_{22}O$ : C, 85·7 ; H, 8·3%).

The *p*-toluenesulphonate formed shining colourless plates from ethanol-ether, m.p. 176 °C (Found : C, 74·0 ; H, 6·6%. Calc. for $C_{26}H_{28}O_3S$ : C, 74·3 ; H, 6·7%).

(xvii) *1-Ethyl-6-methylpyrene.*—The carbinol was dehydrogenated by the usual procedure but the product was difficult to purify. It was converted to the trinitrobenzene adduct which was recrystallized from benzene-ethanol giving orange needles (60% yield), m.p. and mixed m.p. 220 °C (Found : C, 65·4 ; H, 4·0%).

Regeneration of the hydrocarbon was effected by heating with stannous chloride and hydrochloric acid in ethanol. It then crystallized from glacial acetic acid in very pale yellow needles, m.p. and mixed m.p. with the product of (xiii) above, 145 °C (Found : C, 93·1 ; H, 6·6%).

The adduct with 2,4,7-trinitrofluorenone formed red-brown needles from glacial acetic acid, m.p. and mixed m.p. 189 °C (decomp.) (Found : C, 68·3 ; H, 3·9%).

(xviii) *1,6-Diethylpyrene.*—(1) Clemmensen reduction of 1-acetyl-6-ethylhexahydropyrene and purification of the crude product by chromatography on alumina in light petroleum gave 1,6-diethylhexahydropyrene which formed colourless needles (80% yield), m.p. 129 °C, from ethanol (Found : C, 90·7 ; H, 9·3%. Calc. for $C_{20}H_{24}$ : C, 90·9 ; H, 9·1%).

Dehydrogenation of this substance afforded 1,6-diethylpyrene, which formed shining colourless plates from ethanol-benzene, m.p. 179 °C (Found : C, 93·1 ; H, 7·0%. Calc. for $C_{20}H_{18}$ : C, 93·0 ; H, 7·0%).

The trinitrobenzene complex, orange-red needles from ethanol-benzene, had m.p. 217 °C (Found : C, 66·2 ; H, 4·5%. Calc. for $C_{26}H_{21}O_6N_3$ : C, 66·2 ; H, 4·5%).

The picrate crystallized from ethanol in red needles, m.p. 176 °C (Found : C, 64·2 ; H, 4·6%. Calc. for $C_{26}H_{21}O_7N_3$ : C, 64·1 ; H, 4·3%).

(2) Bromine (3·2 g) in carbon disulphide (30 ml) was added with stirring to a solution of 1-ethylhexahydropyrene (4·75 g) in carbon disulphide (30 ml) during 0·25 hr. After keeping for 1 hr, the solvent was removed and the residue extracted several times with hot ethanol, much resinous material remaining undissolved. Concentration of the extracts furnished 1-bromo-6-ethylhexahydropyrene as colourless needles (1·6 g), m.p. 140 °C (Found : C, 68·3 ; H, 6·1%. Calc. for $C_{18}H_{19}Br$ : C, 68·6 ; H, 6·1%).

Ethereal butyl lithium (approx. 0·005 mol) was added to a solution of the bromo compound (0·95 g ; 0·003 mol) in ether (50 ml). After 0·6 hr at room temperature, ethyl iodide (0·8 g)

was added and reaction allowed to proceed for 0·3 hr. Water was cautiously added, the ether layer separated, washed, dried, and evaporated. The residue on dehydrogenation in the usual manner gave 1,6-diethylpyrene (0·33 g), m.p. and mixed m.p. 179 °C.

*(d) The 1,7-Series*

(i) *α,4-(10-Methyl-1,2,3,4-tetrahydrophenanthrylidene)propionic Acid.* — The Reformatsky reaction between the ketone II (10·5 g) and ethyl α-iodopropionate (10 ml) was conducted in the usual manner. Unreacted ketone (3·0 g) was recovered by Girard's Reagent P. The oily ester was dehydrated with phosphorus oxychloride and the resulting unsaturated ester hydrolysed to the acid which crystallized from aqueous ethanol in colourless plates (5·2 g), m.p. 171 °C (decomp.) (Found : C, 81·0 ; H, 6·9%. Calc. for $C_{18}H_{18}O_2$ : C, 81·2 ; H, 6·8%).

(ii) *1-Keto-2,6-dimethyl-1,2,2a,3,4,5-hexahydropyrene.*—Catalytic hydrogenation of the above acid (5·0 g) gave a saturated acid which had little tendency to crystallize. It was converted to the acid chloride which was cyclized by stannic chloride by the standard procedure. The pale yellow product separated from ethanol as a mixture of needles and prisms (yield 75%) which melted over the range, 115–170 °C (Found : C, 86·6 ; H, 7·1%. Calc. for $C_{18}H_{18}O$ : C, 86·4 ; H, 7·3%).

(iii) *1,7-Dimethylpyrene.*—The above ketone (1·0 g) was reduced in ethereal solution by excess lithium aluminium hydride. The crude product on dehydrogenation afforded the required hydrocarbon which formed colourless needles (0·52 g) from ethanol, m.p. 121 °C (Found : C, 93·7 ; H, 5·9%. Calc. for $C_{18}H_{14}$ : C, 93·9 ; H, 6·1%).

The trinitrobenzene adduct separated from ethanol-benzene in orange needles, m.p. 256 °C (Found : C, 65·0 ; H, 3·9%. Calc. for $C_{24}H_{17}O_6N_3$ : C, 65·0 ; H, 3·9%).

The picrate crystallized from ethanol in red needles, m.p. 231 °C (decomp.) (Found : C, 62·7 ; H, 4·0%. Calc. for $C_{24}H_{17}O_7N_3$ : C, 62·7 ; H, 3·7%).

(iv) *1,2,6-Trimethylpyrene.*—Reaction of the ketone III (R=$CH_3$) with methylmagnesium iodide afforded 1,2,6-trimethyl-2*a*,3,4,5-tetrahydropyrene which formed very pale yellow plates from ethanol, m.p. 139–141 °C (Found : C, 91·6 ; H, 8·1%. Calc. for $C_{19}H_{20}$ : C, 91·9 ; H, 8·1%).

Dehydrogenation yielded 1,2,6-trimethylpyrene, colourless needles from ethanol, m.p. 173 °C (Found : C, 93·2 ; H, 6·6%. Calc. for $C_{19}H_{16}$ : C, 93·4 ; H, 6·6%).

The trinitrobenzene adduct formed orange-red needles from benzene-ethanol, m.p. 274 °C (decomp.) (Found : C, 65·6 ; H, 4·4%. Calc. for $C_{25}H_{19}O_6N_3$ : C, 65·6 ; H, 4·2%).

The picrate separated from ethanol in red-brown needles, m.p. 246 °C (decomp.) (Found : C, 63·5 ; H, 4·2%. Calc. for $C_{25}H_{19}O_7N_3$ : C, 63·4 ; H, 4·1%).

(v) *1-Ethyl-2,6-dimethylpyrene.*—Direct dehydrogenation of the product from the ketone III (R=$CH_3$) and ethylmagnesium iodide gave the hydrocarbon (55% yield), colourless needles from ethanol, m.p. 122 °C (Found : C, 92·8 ; H, 7·1%. Calc. for $C_{20}H_{18}$ : C, 93·0 ; H, 7 0%) The mixed m.p. with 1,7-dimethylpyrene (m.p. 121 °C) was 90–95 °C.

The trinitrobenzene adduct crystallized from benzene-ethanol in orange-red needles, m.p. 247 °C (Found : C, 65·9 ; H, 4·5%. Calc. for $C_{26}H_{21}O_6N_3$ : C, 66·2 ; H, 4·5%).

The picrate formed red-brown needles from ethanol, m.p. 223 °C (decomp.) (Found : C, 63·8 ; H, 4·4%. Calc. for $C_{26}H_{21}O_7N_3$ : C, 64·1 ; H, 4·3%).

(vi) *α,4-(10-Methyl-1,2,3,4-tetrahydrophenanthrylidene)butyric Acid.*—By using ethyl α-iodobutyrate and proceeding as in (i) above the ketone II (10·5 g) gave recovered ketone (2·3 g) and acid (6·0 g) which crystallized from methanol in colourless plates, m.p. 169 °C (decomp.) (Found : C, 81·4 ; H, 7·2%. Calc. for $C_{19}H_{20}O_2$ : C, 81·4 ; H, 7·2%).

(vii) *α,4-(10-Methyl-1,2,3,4-tetrahydrophenanthryl)butyric Acid.*—Catalytic hydrogenation of the unsaturated acid furnished the saturated acid, colourless needles, m.p. 135 °C, from hexane (Found : C, 80·7 ; H, 7·6%. Calc. for $C_{19}H_{22}O_2$ : C, 80·8 ; H, 7·9%).

(viii) *1-Keto-2-ethyl-7-methyl-1,2,2a,3,4,5-hexahydropyrene.*—Conversion of the above acid (5 g) to the acid chloride by thionyl chloride followed by cyclization with stannic chloride yielded the ketone III (R=$C_2H_5$) (3·1 g) which crystallized from ethyl acetate in pale yellow prisms, m.p. 191–194 °C (Found : C, 86·1 ; H, 7·7%. Calc. for $C_{19}H_{20}O$ : C, 86·3 ; H, 7·6%).

(ix) *1-Ethyl-7-methylpyrene.*—The carbinol resulting from the reduction of the ketone III (R=$C_2H_5$) (1 g) with lithium aluminium hydride was dehydrogenated directly. The product crystallized from ethanol in colourless plates (0·2 g), m.p. 94 °C (Found : C, 93·1 ; H, 6·5%. Calc. for $C_{19}H_{16}$ : C, 93·4 ; H, 6·6%).

The trinitrobenzene adduct formed orange needles from benzene-ethanol, m.p. 220 °C (Found : C, 65·5 ; H, 4·2%. Calc. for $C_{25}H_{19}O_6N_3$ : C, 65·6 ; H, 4·2%).

(x) *1-Ethyl-2,7-dimethylpyrene.*—Dehydrogenation of the product from the ketone III (R=$C_2H_5$) (1 g) and methylmagnesium iodide gave the hydrocarbon (0·7 g) which separated from ethanol as colourless needles, m.p. 123 °C (Found : C, 92·8 ; H, 7·0%. Calc. for $C_{20}H_{18}$ : C, 93·0 ; H, 7·0%).

The trinitrobenzene adduct crystallized in orange-red needles, m.p. 249–250 °C, from benzene-ethanol (Found : C, 66·0 ; H, 4·6%. Calc. for $C_{26}H_{21}O_6N_3$ : C, 66·2 ; H, 4·5%).

(xi) *1,2-Diethyl-6-methylpyrene.*—The substance, obtained by the usual procedure, formed colourless needles, m.p. 104 °C, from ethanol (Found : C, 92·6 ; H, 7·4%. Calc. for $C_{21}H_{20}$ : C, 92·6 ; H, 7·4%).

The trinitrobenzene adduct separated from benzene-ethanol in orange-red needles, m.p. 225 °C (Found : C, 66·8 ; H, 4·8%. Calc. for $C_{27}H_{23}O_6N_3$ : C, 66·8 ; H, 4·8%).

(xii) *Dimethyl Hexahydropyrene-1,7-dicarboxylate.*—The ester obtained from the acid by the action of excess ethereal diazomethane crystallized from methanol in colourless needles, m.p. 109 °C (Found : C, 74·0 ; H, 6·5%. Calc. for $C_{20}H_{20}O_4$ : C, 74·1 ; H, 6·2%).

(xiii) *1,7-Bishydroxymethylhexahydropyrene.*—Reduction of the ester (0·8 g) by lithium aluminium hydride in ether using the Soxhlet technique gave the product which formed cream plates (0·5 g), m.p. 196 °C, from aqueous ethanol (Found : C, 80·2 ; H, 7·3%. Calc. for $C_{18}H_{20}O_2$ : C, 80·6 ; H, 7·5%).

(xiv) *1,7-Dimethylpyrene.*—Dehydrogenation of the diol (0·5 g) by the standard method gave the hydrocarbon which separated from ethanol in colourless needles (0·06 g), m.p. 120 °C, undepressed by admixture with the substance prepared in (iii) above (Found : C, 93·6 ; H, 6·1%. Calc. for $C_{18}H_{14}$ : C, 93·9 ; H, 6·1%). The trinitrobenzene adduct, orange needles from ethanol, had m.p. 256 °C, undepressed by admixture with the adduct from (iii) (Found : C, 65·0 ; H, 4·0%. Calc. for $C_{24}H_{17}O_6N_3$ : C, 65·0 ; H, 3·9%).

(xv) *1,7-Diethylpyrene.*—Clemmensen reduction of 1,7-diacetylhexahydropyrene (2·9 g) by the standard procedure furnished 1,7-diethylhexahydropyrene (2·1 g), which crystallized from ethanol in colourless needles, m.p. 92 °C (Found : C, 91·0 ; H, 9·2%. Calc. for $C_{20}H_{24}$ : C, 90·9 ; H, 9·1%).

Dehydrogenation of this substance then gave the required hydrocarbon which separated from ethanol as colourless needles, m.p. 128 °C (Found : C, 92·7 ; H, 7·1%. Calc. for $C_{20}H_{18}$ : C, 93·0 ; H, 7·0%).

The trinitrobenzene adduct formed orange needles, m.p. 199 °C, from ethanol (Found : C, 66·2 ; H, 4·5%. Calc. for $C_{26}H_{21}O_6N_3$ : C, 66·2 ; H, 4·5%).

(xvi) *1-Acetylhexahydropyrene-7-carboxylic Acid.*—A mixture of diacetylhexahydropyrene (9·7 g), iodine (8·5 g), and pyridine (35 ml) was heated on the water-bath for 2 hr and then kept overnight. Excess pyridine was removed under reduced pressure and the residue triturated successively with boiling benzene (3×75 ml) and with water (4×40 ml). From the former extract, starting material (3·4 g) was recovered.

The undissolved material was heated on the water-bath for 2 hr with water (200 ml) and sodium hydroxide (10 g). The reaction mixture was cooled, acidified, and the crude product collected. It was dissolved in hot dilute sodium carbonate, the solution charcoaled, filtered,

cooled, and carefully acidified. A brown resin which separated first was filtered off and then the product (5·0 g) was precipitated. It crystallized from toluene in cream microneedles, m.p. 238 °C (Found: C, 77·4; H, 6·1%. Calc. for $C_{19}H_{18}O_3$: C, 77·5; H, 6·2%).

The methyl ester separated from methanol in colourless needles, m.p. 78 °C (Found: C, 77·4; H, 6·7%. Calc. for $C_{20}H_{20}O_3$: C, 77·9; H, 6·5%).

The dinitrophenylhydrazone of the methyl ester formed bright yellow needles, m.p. 228 °C from benzene (Found: C, 63·6; H, 5·0%. Calc. for $C_{26}H_{24}O_6N_4$: C, 63·9; H, 5·0%).

(xvii) *Methyl 1-Ethylhexahydropyrene-7-carboxylate.*—Clemmensen reduction of the above ester (3·1 g) in the presence of toluene in the usual manner did not effect hydrolysis to any important extent. The toluene layer was washed with water, dilute sodium carbonate, and again with water. After removing the solvent the residue was purified by chromatography in light petroleum on alumina. The ester crystallized from methanol in colourless needles (2·5 g), m.p. 54 °C (Found: C, 81·3; H, 7·5%. Calc. for $C_{20}H_{22}O_2$: C, 81·6; H, 7·5%).

The acid, obtained by alkaline hydrolysis, formed colourless needles from ethanol, m.p. 234 °C (Found: C, 81·2; H, 7·2%. Calc. for $C_{19}H_{20}O_2$: C, 81·4; H, 7·2%).

(xviii) *1-Ethyl-7-hydroxymethylhexahydropyrene.*—Reduction of the above ester (2·1 g) by lithium aluminium hydride in ether afforded the carbinol which formed colourless needles (1·6 g), m.p. 151 °C from aqueous ethanol (Found: C, 85·4; H, 8·3%. Calc. for $C_{19}H_{22}O$: C, 85·7; H, 8·3%).

(xix) *1-Ethyl-7-methylpyrene.*—Dehydrogenation of the carbinol (1·2 g) in the usual manner gave the hydrocarbon (0·9 g) which crystallized from ethanol in colourless plates, m.p. 94 °C, alone or mixed with the substance prepared in (ix) above.

The trinitrobenzene adduct, orange needles from benzene-ethanol, had m.p. 220 °C undepressed by admixture of the adduct of (ix) above.

## VIII. Acknowledgments

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# THE SYNTHESIS OF FUROQUINOLINE ALKALOIDS: DICTAMNINE AND EVOLITRINE

By R. G. Cooke* and H. F. Haynes*

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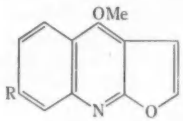
*Summary*

The previously outlined synthesis of dictamnine is now described completely. The analogous synthesis of evolitrine proves that it is 7-methoxydictamnine.

## I. Introduction

In an earlier paper (Cooke and Haynes 1954) the structure I (R=OMe) was assigned to evolitrine, a new furoquinoline alkaloid from *Evodia litoralis* Endl. The linear arrangement of the ring system was assumed by analogy with the accepted structures for dictamnine (I; R=H) and kokusaginine because the absorption spectra of the three alkaloids are very similar.




(I)

At that time no synthesis of a furoquinoline alkaloid had been published and the linear structure was based largely on negative evidence (much of which was subsequently shown to be erroneous). Accordingly the synthesis of dictamnine and evolitrine was undertaken. Since then much evidence for the linear structure has been obtained and has been reviewed by Price (1956), who also reported the outline of our synthesis of dictamnine up to the penultimate stage. In the meantime different syntheses of dictamnine and γ-fagarine have been published by Böhm and Tuppy (1956*a*, 1956*b*) and by Grundon and McCorkindale (1957). Another independent synthesis of dictamnine was reported by Sato and Ohta (1956), and dihydroskimmianine has been obtained by Ohta and Mori (1957).†

## II. Details of the Synthesis of Dictamnine and Evolitrine

The appropriate anthranilic ester was converted to the succinanilic ester II (R=H or OMe) by reaction with succinic anhydride and subsequent esterification with diazomethane. Cyclization with sodium (Camps synthesis) then gave

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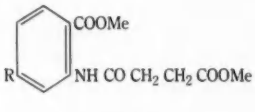
† Ohta and Mori (*Ann. Rep. Tokyo Coll. Pharm.* **7**: 38 (1957)) have also reported a synthesis of dihydroevolitrine.

the hydroxyquinolone ester III and another product believed to be IV. Initially, the ethyl ester corresponding to III (R=H) was obtained by direct condensation of methyl anthranilate and diethyl succinate in the presence of sodium, but this method was less satisfactory.

The compound III was methylated by diazomethane to give the 4-methoxy-2-quinolone which was then reduced with lithium aluminium hydride to the primary alcohol V. Cyclization to the dihydrofuroquinoline was effected by heating with polyphosphoric acid but, in the case of dihydroevolitrine (VI; R=OMe), better results were obtained by converting the alcohol to the chloride and then cyclizing with silver oxide. Finally, the dihydrofuroquinolines were brominated with *N*-bromosuccinimide and then hydrogen bromide was removed by boiling collidine. The two products (I; R=H and I; R=OMe) were identical, respectively, with natural dictamnine and evolitrine.

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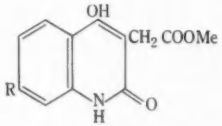


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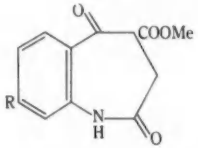


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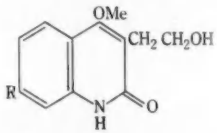


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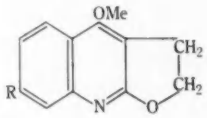


(VI)

This method should be suitable for the synthesis of other furoquinolines if the appropriate anthranilic acids are accessible. Some of these are readily obtained by oxidation of the corresponding isatins which are conveniently prepared by using polyphosphoric acid in the last stage of the Sandmeyer synthesis (Piozzi and Favini 1955).

## III. Experimental

Melting points are corrected. Microanalyses by Dr. W. Zimmermann and assistants.

### (*a*) *Synthesis of Dictamnine*

(i) o-*Methoxycarbonylsuccinanilic Acid.*—Methyl anthranilate (11 g) and succinic anhydride (6 g) were heated together in boiling benzene (150 ml) for 10 min. The *succinanilic acid* (11·2 g, m.p. 130–132 °C) separated from the cooled solution. It was recrystallized from methanol as prisms, m.p. 136–136·5 °C (Found: C, 57·8; H, 5·3; N, 5·6%. Calc. for $C_{12}H_{13}O_5N$: C, 57·4; H, 5·2; N, 5·6%). The *methyl ester* (*II*; *R=H*) was prepared by the action of diazomethane in ether. It crystallized from light petroleum as needles, m.p. 72–72·5 °C (Found: C, 59·3; H, 5·7%. Calc. for $C_{13}H_{15}O_5N$: C, 58·9; H, 5·7%).

(ii) *Methyl 4-Hydroxy-2-quinolone-3-acetate* (*III*; *R=H*).—The above methyl ester (4·5 g), finely-divided sodium (0·6 g), and dry toluene (20 ml) were heated on the water-bath until the

reaction had ceased. The precipitate of sodium salts was collected, washed with light petroleum, dried, and then dissolved in water. The solution was extracted with ether and then neutralized with acetic acid to precipitate fraction *A* (0·4 g). Further addition of acetic acid to the filtrate precipitated fraction *B* (1·2 g, 30%). Fraction *A* was crystallized from methanol to give the *keto-ester* (*IV*; *R*=*H*) in needles, m.p. 225–226 °C (Found: C, 62·3; H, 4·8; N, 5·9%. Calc. for $C_{12}H_{11}O_4N$: C, 61·8; H, 4·8; N, 6·0%). The compound gave a purple colour with ferric chloride in aqueous ethanol, and with diazomethane in ether it formed a *methyl ether* which separated from water as needles, m.p. 149·5–150 °C (Found: C. 63·0; H, 5·2; N, 5·5; OMe, 23·5%. Calc. for $C_{13}H_{13}O_4N$: C, 63·2; H, 5·2; N, 5·7; 2×OMe, 25·1%).

Fraction *B* crystallized from methanol to give the *quinolone* (*III*; *R*=*H*) in prisms which did not melt below 320 °C (Found: C, 62·0; H, 4·9; N, 6·4%. Calc. for $C_{12}H_{11}O_4N$: C, 61·8; H, 4·8; N, 6·0%). This product gives no colour with ferric chloride.

(iii) *Methyl 4-Methoxy-2-quinolone-3-acetate.*—The hydroxyquinolone was methylated by brief treatment with diazomethane in ether. The *product* crystallized from methanol as needles, m.p. 171–171·5 °C (Found: C, 63·5; H, 5·3; N, 5·6%. Calc. for $C_{13}H_{13}O_4N$: C, 63·2; H, 5·2; N, 5·7%).

(iv) *3β-Hydroxyethyl-4-methoxy-2-quinolone* (*V*; *R*=*H*).—The above ester (1·4 g) was reduced with lithium aluminium hydride (0·3 g) in boiling ether (250 ml) for 4 hr. The excess hydride was destroyed with methanol and the mixture was added to 2N sulphuric acid (20 ml). Most of the product separated in needles and more was obtained by evaporating the ether (total yield 72%). The *alcohol* crystallized from water as needles, m.p. 182–182·5 °C (Found: C, 65·5; H, 5·8; OMe, 14·0%. Calc. for $C_{12}H_{13}O_3N$: C, 65·7; H, 5·9; 1×OMe, 14·2%).

(v) *Dihydrodictamnine* (*VI*; *R*=*H*).—The above alcohol (200 mg) and polyphosphoric acid (85%; 5 ml) were heated at 120–122 °C for 75 min. The reaction mixture was poured into water and the resulting solution was basefied and extracted with chloroform. The solvent was evaporated and the solid residue was extracted repeatedly with light petroleum from which the dihydrodictamnine (140 mg, m.p. 102–103 °C) was recovered. After crystallization from benzene-light petroleum it was obtained as needles, m.p. 104–104·5 °C, alone or mixed with authentic dihydrodictamnine (Found: C, 71·8; H, 5·8; N, 6·9%. Calc. for $C_{12}H_{11}O_2N$: C, 71·6; H, 5·5; N, 7·0%. Light absorption in ethanol: $\lambda_{max.}$ (mμ) 320, 307·5, *297·5*, 282·5, 271·5, 262·5, *252·5*, *237·5*, 228·5; log $\varepsilon_{max.}$ 3·65, 3·58, *3·34*, 3·75, 3·83, 3·75, *3·60*, *4·53*, 4·67 (italicized values represent inflexions).

By heating with excess methyl iodide in a sealed tube for 4 hr at 100 °C it was converted to *dihydroisodictamnine* which crystallized from water in needles, m.p. 137–137·5 °C (Found: C, 71·4; H, 5·4; OMe, nil; NMe, 6·9%. Calc. for $C_{12}H_{11}O_2N$: C, 71·6; H, 5·5; 1×NMe, 7·5%).

(vi) *Dictamnine* (*I*; *R*=*H*).—Dihydrodictamnine (30 mg), *N*-bromosuccinimide (27 mg), benzoyl peroxide (1 mg), and anhydrous sodium acetate (200 mg) were heated under reflux in carbon tetrachloride (10 ml) and acetic acid (1 ml) for 4 hr. The mixture was poured into sodium hydroxide solution (2%), separated, and the carbon tetrachloride solution was washed with water. Evaporation of the solvent under reduced pressure gave a pale yellow oil which was boiled with collidine (5 ml) for 6 hr. The solvent was then evaporated and the brown residue was purified by chromatography over alumina in benzene. The dictamnine (20 mg, m.p. 130–131 °C) was further purified by crystallization from aqueous methanol. It formed needles, m.p. 132–132·5 °C, alone or mixed with natural dictamnine (Found: C, 72·3; H, 4·6; N, 7·2%. Calc. for $C_{12}H_9O_2N$: C, 72·4; H, 4·6; N, 7·0%). The picrate separated from methanol as yellow plates, m.p. 164–165 °C, alone or mixed with authentic dictamnine picrate.

(vii) *Condensation of Methyl Anthranilate with Diethyl Succinate.*—Methyl anthranilate (25 g), ethyl succinate (58 g), and finely-divided sodium (2·4 g) were heated on the water-bath until all the sodium had reacted. The mixture was cooled and acetic acid (12 ml) was added. After 48 hr ether was added and the precipitate was separated by decantation and trituration with fresh ether until a solid product was obtained. Extraction of the combined ethereal solutions with hydrochloric acid (2%) caused the separation of more of the product. Total yield 20%. The *ethyl 4-hydroxy-2-quinolone-3-acetate* crystallized from methanol as fine needles which did

not melt below 320 °C (Found: C, 63·3; H, 5·6; N, 5·7%. Calc. for $C_{13}H_{13}O_4N$: C, 63·3; H, 5·3; N, 5·7%).

Brief treatment of this product with diazomethane in ether gave *ethyl 4-methoxy-2-quinolone-3-acetate* which separated from aqueous methanol in needles, m.p. 154–154·5 °C (Found: C, 64·5; H, 5·9; N, 5·2%. Calc. for $C_{14}H_{15}O_4N$: C, 64·5; H, 5·8; N, 5·3%).

Reduction of this ester with lithium aluminium hydride as in (iv) gave the same product, 3β-hydroxyethyl-4-methoxy-2-quinolone, m.p. and mixed m.p. 182–182·5 °C.

*(b) Synthesis of Evolitrine*

Experimental details are omitted when preparations are similar to those in the dictamnine series.

(i) *Methyl 4-Methoxyanthranilate.*—*m*-Methoxy*iso*nitrosoacetanilide (5 g) was added gradually with stirring to polyphosphoric acid (80%; 25 ml) at 55–60 °C and this temperature was then maintained for 10 min. The cooled mixture was poured into water and the precipitated 4-methoxyisatin (4 g) was purified as described by Marvel and Hiers (1941) and crystallized from ethanol, m.p. 226–228 °C; yield 75%.

Hydrogen peroxide (3%; 9 ml) was added slowly to a cooled solution of the crude isatin (1 g) and sodium hydroxide (1 g) in water (7 ml). After standing for 30 min the mixture was neutralized with concentrated hydrochloric acid and then acidified with acetic acid. The acid was precipitated as light brown needles, m.p. 176–178 °C; yield 85%. This material was converted directly to the *methyl ester* which crystallized from light petroleum as needles, m.p. 78·5–79 °C (Found: C, 59·9; H, 6·0%. Calc. for $C_9H_{11}O_3N$: C, 59·7; H, 6·1%).

(ii) *2-Methoxycarbonyl-5-methoxysuccinanilic Acid.*—This *acid* (79% yield) crystallized from methanol as prisms, m.p. 148–148·5 °C (Found: C, 55·6; H, 5·3; N, 5·2%. Calc. for $C_{13}H_{15}O_6N$: C, 55·5; H, 5·4; N, 5·0%).

The *methyl ester* (*II*; *R*=*OMe*) crystallized from light petroleum as needles, m.p. 108–108·5 °C (Found: C, 57·3; H, 5·7%. Calc. for $C_{14}H_{17}O_6N$: C, 57·0; H, 5·8%).

(iii) *Methyl 4-Hydroxy-7-methoxy-2-quinolone-3-acetate* (*III*; *R*=*OMe*).—The Camps synthesis gave two products. The *keto-ester* (*IV*; *R*=*OMe*) was obtained in 14% yield and crystallized from methanol as fine needles, m.p. 246–246·5 °C (Found: C, 59·6; H, 5·1; N, 5·6%. Calc. for $C_{13}H_{13}O_5N$: C, 59·3; H, 5·0; N, 5·3%). It gave a red-brown colour with ferric chloride in aqueous ethanol.

The *quinolone* (*III*; *R*=*OMe*) was obtained in 37% yield and crystallized from methanol as prisms which did not melt below 320 °C (Found: C, 59·6; H, 5·2; N, 5·1%. Calc. for $C_{13}H_{13}O_5N$: C, 59·3; H, 5·0; N, 5·3%). It gave no colour with ferric chloride.

(iv) *Methyl 4,7-Dimethoxy-2-quinolone-3-acetate.*—The *methyl ether* separated from water or benzene-light petroleum as needles, m.p. 183–183·5 °C (Found: C, 61·0; H, 5·6%. Calc. for $C_{14}H_{15}O_5N$: C, 60·6; H, 5·5%).

(v) *3β-Hydroxyethyl-4,7-dimethoxy-2-quinolone* (*V*; *R*=*OMe*).—The ester was treated with a threefold excess of lithium aluminium hydride in tetrahydrofuran at room temperature for 2 hr. The excess hydride was decomposed and the solvent was removed under reduced pressure. Ether and 2N sulphuric acid were added and the required *alcohol* separated in 52% yield, m.p. 175–176·5 °C. It formed needles from benzene, m.p. 176–176·5 °C (Found: C, 62·6; H, 6·0; N, 5·7; OMe, 24·0%. Calc. for $C_{13}H_{15}O_4N$: C, 62·6; H, 6·1; N, 5·6; 2×OMe, 24·9%).

(vi) *Dihydroevolitrine* (*VI*; *R*=*OMe*).—The alcohol (40 mg) was heated with a previously aerated mixture of phosphorus oxychloride (4·8 ml) and water (0·1 ml) at 110 °C for 3 hr. The phosphorus oxychloride was then removed, water was added, and the mixture was basefied with sodium carbonate and extracted with chloroform. After evaporation of the solvent the residue was dissolved in ethanol (5 ml) and water (3·5 ml) and heated under reflux for 2 hr with silver oxide (from 24 mg of silver nitrate). The filtered solution was evaporated to dryness under reduced pressure and the residue was purified by chromatography over alumina in benzene. The *dihydroevolitrine* was eluted with benzene containing 0·5% ethanol. Yield 70%, m.p. 134–136 °C.

After sublimation and crystallization from aqueous methanol it was obtained as needles, m.p. 137–137·5 °C (Found: C, 67·4; H, 5·7; N, 6·0%. Calc. for $C_{13}H_{12}O_3N$: C, 67·5; H, 5·7; N, 6·1%).

(vii) *Evolitrine.*—The synthetic alkaloid was obtained in 59% yield by bromination/dehydrobromination of the dihydroevolitrine and was purified by chromatography. It crystallized from light petroleum as needles, m.p. 114–115 °C, alone or mixed with natural evolitrine (Found: C, 67·6; H, 4·8; OMe, 25·9%. Calc. for $C_{13}H_{11}O_3N$: C, 68·1; H, 4·8; 2×OMe, 27·1%). The picrate formed pale yellow needles from ethanol, m.p. 201–202 °C, alone or mixed with authentic evolitrine picrate. In Cooke and Haynes's (1954) earlier paper, the m.p. of this derivative was erroneously recorded as 191–192 °C.

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# COLOURING MATTERS OF AUSTRALIAN PLANTS

## VI. HAEMOCORIN : THE STRUCTURE OF THE AGLYCONE

By R. G. Cooke,* B. L. Johnson,* and W. Segal*

[*Manuscript received January* 24, 1958]

*Summary*

Some model mono- and dihydroxy*peri*naphthenones have been prepared for comparison with the natural colouring matter. Their properties indicate that haemocorin is most probably a derivative of 2,5,6-trihydroxy*peri*naphthenone. In particular 6-hydroxy-7(or 9)-phenyl*peri*naphthenone evidently includes the main features of the chromophore, but the extra oxygen substituents in the aglycone must have a strong auxochromic effect. The complete structure has been finally established by decarboxylation of the two dimethoxyphenylnaphthalic anhydrides previously obtained by oxidation of the isomeric dimethyl ethers. The products have been identified by synthesis as 1,2-dimethoxy-6-phenylnaphthalene and 1,2-dimethoxy-8-phenylnaphthalene. The aglycone is therefore formulated as 2,6-dihydroxy-5-methoxy-9-phenyl*peri*naphthenone-1 although this structure is potentially tautomeric.

### I. Introduction

In Part V of this series (Cooke and Segal 1955) the aglycone from haemocorin was recognized as a dihydroxymethoxyphenyl*peri*naphthenone. Three possible distributions of the oxygen substituents were suggested and for each of these there were two possible positions for the phenyl group. Each of these six possible structures was also potentially tautomeric and no particular arrangement was established. Some simple model compounds gave certain indications of structure but they were not sufficiently comparable to allow any definite conclusions.

### II. New Model *peri*Naphthenones

To provide more satisfactory models for comparison, and to explore possible approaches to the synthesis of the aglycone, several new hydroxy*peri*naphthenones have been prepared. A process previously used for preparing *peri*naphthenone itself (Fieser and Hershberg 1938) has been adapted for the synthesis of 6-hydroxy*peri*naphthenone and some of its derivatives. The condensation of 2,7-dihydroxynaphthalene with glycerol in the presence of phosphoric acid and an oxidizing agent gives the parent 6-hydroxy compound (I). By using cinnamic aldehyde in place of glycerol a low yield of 6-hydroxy-7(or 9)-phenyl*peri*naphthenone (II) is obtained.

The required dihydroxy*peri*naphthenones are readily prepared from 4- and 6-methoxy*peri*naphthanones by condensation with *p*-nitrosodimethylaniline followed by acid hydrolysis. In the last step demethylation occurs, as well as replacement of the anilino group, and the respective products are 2,4-dihydroxy-

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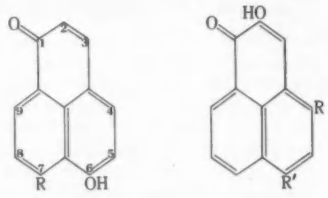
*peri*naphthenone (III) and the 2,6-isomer (IV). Unlike the aglycone and some other unsymmetrically substituted compounds in this series, these two substances give only one dimethyl ether.

The colour reactions and light absorption of these compounds and their ethers (Section IV), together with others previously described (Cooke and Segal 1955), show that the different arrangements of oxygen substituents can be clearly




(I; R = H) (III; R = OH; R′ = H)
(II; R = Ph) (IV; R = H; R′ = OH)

distinguished and that the aglycone is most probably a derivative of 2,5,6-trihydroxy*peri*naphthenone. For 6-hydroxy-7(or 9)-phenyl*peri*naphthenone the shape of the absorption curve is very similar to those obtained for the aglycone and its derivatives, but extra oxygen substituents evidently have a strong auxochromic effect.

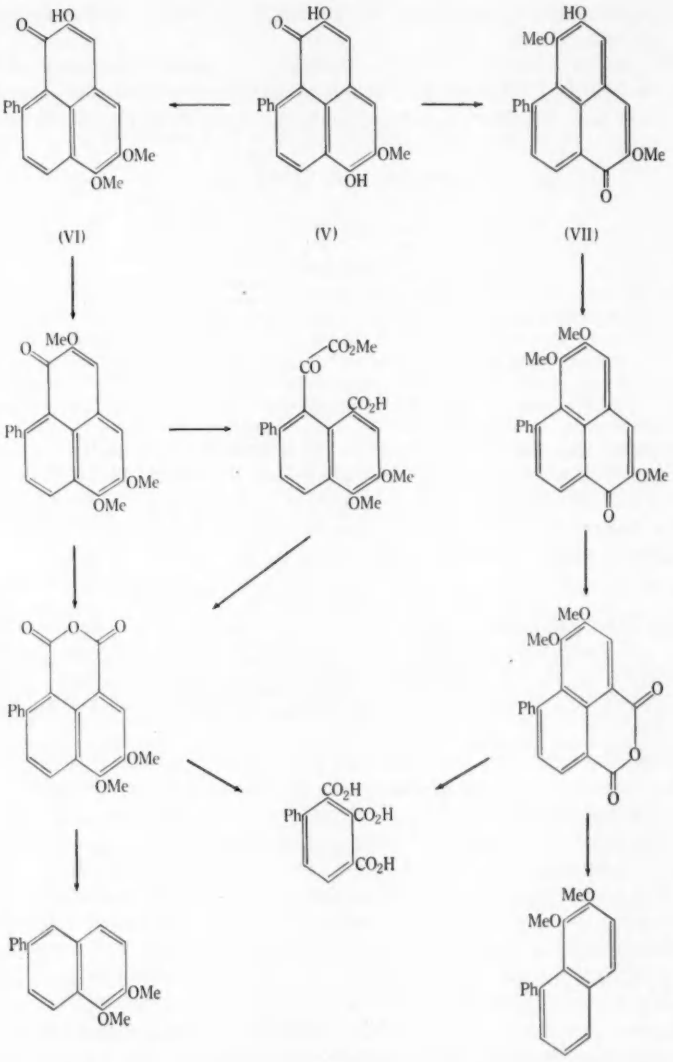
## III. The Structure of the Aglycone

The most promising method for final elucidation of the structure seemed to be decarboxylation of the two dimethoxyphenylnaphthalic anhydrides previously obtained by oxidation of the aglycone dimethyl ethers. This was accomplished by a two-stage process involving a mercuration reaction as described by Davies, Heilbron, and Irving (1932).

From the preceding evidence only two structures seem possible for the resulting dimethoxyphenylnaphthalenes. However, if the other arrangements of the oxygen substituents in the pigment are not excluded, two additional structures must be considered. Only one of these compounds, 6,7-dimethoxy-1-phenylnaphthalene, has been described previously in the literature. Samples of all four were eventually synthesized and in this way the degradation product derived from the aglycone dimethyl ether A was identified as 1,2-dimethoxy-6-phenylnaphthalene, whilst that from dimethyl ether B was proved to be 1,2-dimethoxy-8-phenylnaphthalene. The dimethoxyphenylnaphthalenes are easily identified by their distinctive absorption spectra (Section IV).

Monomethyl ether A and dimethyl ether A are both oxidized to the same anhydride which therefore must contain the methoxyl group originally present in the pigment.

All these results establish that the aglycone is 2,6-dihydroxy-5-methoxy-9-phenyl*peri*naphthenone (V). Tautomerism may be possible, but as internal hydrogen bonding would be expected to stabilize the structure V, it seems acceptable as the formula of the pigment.




The position and stereochemistry of the glycoside link in haemocorin have not been determined. However, as the light absorption of the glycoside resembles that of the aglycone monomethyl ether B, rather than monomethyl ether A, the sugar is presumably not attached at position 6 in structure V.

**The relationship of the aglycone to its various derivatives is shown in the chart. Monomethyl ether A has the structure VI and monomethyl ether B must be VII.**

## IV. Experimental

**Unless otherwise stated all melting points were corrected and observed in Pyrex capillaries. Ultraviolet spectra were measured with a Hilger Uvispek photoelectric spectrophotometer. Microanalyses are by Dr. K. W. Zimmermann and assistants.**

(*a*) *6-Hydroxyperinaphthenone.*—A mixture of 2,7-dihydroxynaphthalene (2 g), sodium nitrobenzenesulphonate (2·5 g), glycerol (5 g), phosphoric acid (98% ; 12 c.c.), ferrous sulphate (0·6 g) and boric acid (1 g) was heated during 10 min to 150 °C and then maintained at 150–170 °C for 35 min. The mixture was then poured into water, warmed to coagulate the precipitate, and filtered. The residue was washed with water and then extracted with hot aqueous sodium carbonate. The magenta coloured filtrate was acidified with hydrochloric acid and the precipitate was collected, washed with water, and dried. Crude yield, 0·6 g. This *product* was sublimed in a high vacuum and crystallized from ethanol as microscopic red needles, m.p. 295–297 °C decomp. (uncorr.) (Found : C, 79·3 ; H, 4·4%. Calc. for $C_{13}H_8O_3$ : C, 79·6 ; H, 4·1%) ; light absorption in ethanol : $\lambda_{max.}$ (mμ) 452·5, 356, 340, 312·5, 298·5, 263·5 ; log $\varepsilon_{max.}$ 4·06, 3·47, 3·25, 3·62, 3·61, 4·32. The compound dissolves readily in aqueous alkalis, giving magenta solutions with strong orange-red fluorescence. It is also obtained by cyclizing β-(4-methoxy-1-naphthyl)propionic acid under conditions which cause dehydrogenation of the resulting saturated ketone (e.g. by heating with polyphosphoric acid).

The *methyl ether* (prepared by the action of dimethyl sulphate and potassium carbonate in acetone) was purified by chromatography on alumina in benzene, sublimation, and crystallization from benzene-light petroleum. It formed orange needles, m.p. 160–161 °C (Found : C, 80·1 ; H, 4·9 ; MeO, 14·8%. Calc. for $C_{14}H_{10}O_3$ : C, 80·0 ; H, 4·8 ; MeO, 14·5%) ; light absorption in ethanol : $\lambda_{max.}$ (mμ) 435, 356, 340, 310, *270*, 261 ; log $\varepsilon_{max.}$ 4·08, 3·53, 3·30, 3·59, *4·18*, 4·28.

(*b*) *6-Hydroxy-7(or 9)-phenylperinaphthenone.*—The preparation was similar to that above but cinnamic aldehyde (4 g) was used in place of glycerol and the boric acid was omitted. The *product* was sublimed in a high vacuum and crystallized from ethanol in small red needles, m.p. 282–284 °C decomp. (uncorr.). In aqueous alkalis it formed red-violet solutions with weak, dull green fluorescence (Found : C, 83·8 ; H, 4·7%. Calc. for $C_{19}H_{12}O_2$ : C, 83·8 ; H, 4·5%) ; light absorption in ethanol : $\lambda_{max.}$ (mμ) 453, 360, *345*, *295*, 266 ; log $\varepsilon_{max.}$ 4·02, 3·68, *3·55*, *4·04*, 4·34.

(*c*) *2,4-Dihydroxyperinaphthenone.*—Crude 4-methoxy*peri*naphthanone (9 g) was prepared as described by Badger, Carruthers, and Cook (1949) and was condensed in ethanol with *p*-nitrosodimethylaniline (6 g) and potassium hydroxide (2·2 g). After about 4 hr at room temperature the almost black precipitate (12 g) was collected and was hydrolysed by heating under a reflux condenser for 4 hr with aqueous-ethanolic hydrochloric acid (approx. 5N). Water was added to the cooled mixture and the dark red precipitate was collected. Part of the material was purified by sublimation in a high vacuum and crystallization from aqueous ethanol. The *2,4-dihydroxyperinaphthenone* forms red needles which decompose without melting when heated. It gives violet solutions in aqueous alkalis (Found : C, 72·8 ; H, 4·0%. Calc. for $C_{13}H_8O_3$ : C, 73·5 ; H, 3·8%). When methylated with dimethyl sulphate and potassium carbonate in acetone it gave *2,4-dimethoxyperinaphthenone* which crystallized from benzene-light petroleum in orange blades, m.p. 169–170 °C (Found : C, 74·8 ; H, 5·0 ; MeO, 25·2%. Calc. for $C_{15}H_{12}O_3$ : C, 75·0 ; H, 5·0 ; 2×MeO, 25·8%) ; light absorption in ethanol : $\lambda_{max.}$ (mμ) 451, *395*, 328·5, *318*, 273 ; log $\varepsilon_{max.}$ 4·04, *3·70*, 3·79, *3·63*, 4·43. The structure of this product was established by oxidation with permanganate in acetone to 2-methoxynaphthalic anhydride, m.p. and mixed m.p. 259–260 °C (micro hot stage).

(*d*) *6-Methoxyperinaphthanone.*—β-(4-Methoxy-1-naphthyl)propionic acid was prepared by hydrogenation of the corresponding acrylic acid in aqueous sodium carbonate with palladium charcoal. The saturated acid (1 g) was converted to the chloride by the action of thionyl chloride.

The crude chloride was dissolved in benzene (30 c.c.) and allowed to react for 1·5 hr with stannic chloride (2 c.c.) at a temperature just above the freezing point of the mixture. Ether was then added and the mixture was poured into ice and concentrated hydrochloric acid. The ether layer was washed with concentrated hydrochloric acid, then with aqueous sodium carbonate, and finally with water. Dilution of the concentrated acid washings gave 6-hydroxy*peri*naphthenone (0·3 g), and acidification of the alkaline washings gave the original acid (0·2 g). The ether layer was dried (magnesium sulphate) and evaporated to give *6-methoxyperinaphthanone* (0·46 g) which crystallized from aqueous methanol in yellow needles, m.p. 75–76 °C (Found: C, 78·9; H, 5·7; MeO, 14·3%. Calc. for $C_{14}H_{12}O_2$: C, 79·2; H, 5·7; MeO, 14·6%).

(*e*) *2,6-Dihydroxyperinaphthenone.*—The crude saturated ketone was condensed with *p*-nitrosodimethylaniline substantially as described in (*c*) above. The crude product (0·5 g) was dissolved in ethanol (10 c.c.) and concentrated hydrochloric acid (10 c.c.) and the mixture was boiled under reflux condenser for 5 hr. After sublimation in vacuum and crystallization from aqueous ethanol the resulting *2,6-dihydroxyperinaphthenone* formed purple needles which decomposed without melting when heated and gave blue solutions in alkalis. Methylation gave *2,6-dimethoxyperinaphthenone* which crystallized from benzene-light petroleum in red prisms, m.p. 142–143 °C (Found: C, 75·3; H, 5·0%. Calc. for $C_{15}H_{12}O_3$: C, 75·0; H, 5·0%); light absorption in ethanol: $\lambda_{max.}$ (mμ) 462, 362, 344, 323·5, *311*, 283, 262·5; log $\varepsilon_{max.}$ 3·96, 3·48, 3·41, 3·74, *3·63*, 4·18, 4·23.

(*f*) *6,7-Dimethoxy-1-phenylnaphthalene.*—This compound was prepared as described by Howell and Robertson (1936) except that sulphur was used in the dehydrogenation stage. The product had m.p. 107·5–108 °C (lit. gives 110 °C). Light absorption in ethanol: $\lambda_{max.}$ (mμ) 325·5, 288, 238; log $\varepsilon_{max.}$ 3·48, 3·88, 4·81.

(*g*) *6,7-Dimethoxy-2-phenylnaphthalene.*—6,7-Dimethoxy-2-phenyl-1-tetralone (Robinson and Young 1935) was reduced by the Clemmensen-Martin procedure. The crude product was dehydrogenated by heating with sulphur at 230 °C for ½ hr and then at 250 °C for ½ hr. After chromatography over alumina in benzene, the product was sublimed in a vacuum and crystallized from ethanol and then aqueous ethanol. The *6,7-dimethoxy-2-phenylnaphthalene* formed blades, m.p. 134–135 °C (Found: C, 82·1; H, 6·3; MeO, 22·8%. Calc. for $C_{18}H_{16}O_2$: C, 81·8; H, 6·1; 2×MeO, 23·4%); light absorption in ethanol: $\lambda_{max.}$ (mμ) 333, 288·5, 252·5; log $\varepsilon_{max.}$ 3·48, 4·18, 4·76.

(*h*) *1,2-Dimethoxy-6-phenylnaphthalene.*—A sample of 6-phenyl-2-naphthol (Hey and Lawton 1940) was converted into 6-phenyl-1,2-naphthoquinone by the general process described by Fieser (1941). The crude quinone (1 g) was treated with acetic anhydride, zinc dust, and triethylamine and the resulting *1,2-diacetoxy-6-phenylnaphthalene* (0·8 g) was crystallized from methanol as plates, m.p. 140–141 °C (Found: C, 75·0; H, 5·1%. Calc. for $C_{20}H_{16}O_4$: C, 75·0; H, 5·0%).

This product (0·5 g) was suspended in methanol (10 c.c.) with excess dimethyl sulphate. Excess aqueous sodium hydroxide was added gradually, with shaking, and the mixture was then boiled for ½ hr under a reflux condenser. The cooled mixture was diluted with water and extracted with ether. The residue from the ether layer was dissolved in benzene and passed over alumina and the recovered *1,2-dimethoxy-6-phenylnaphthalene* crystallized from aqueous ethanol in plates, m.p. 114–115 °C (Found: MeO, 21·4%. Calc. for $C_{18}H_{16}O_2$: 2×MeO, 23·4%); light absorption in ethanol: $\lambda_{max.}$ (mμ) *340*, 300·5, 257·5; log $\varepsilon_{max.}$ *3·35*, 4·01, 4·76.

(*i*) *1,2-Dimethoxy-8-phenylnaphthalene.*—This was prepared from 7-methoxy-1-phenylnaphthalene (Howell and Robertson 1936) by way of 8-phenyl-1,2-naphthoquinone as described for the isomer in (*h*) above. The *1,2-diacetoxy-8-phenylnaphthalene* crystallized from aqueous ethanol in blades, m.p. 139–140 °C (Found: C, 75·1; H, 5·0; MeCO, 26·9%. Calc. for $C_{20}H_{16}O_4$: C, 75·0; H, 5·0; 2×MeCO, 26·8%). The *1,2-dimethoxy-8-phenylnaphthalene* separated from aqueous ethanol in blades, m.p. 88–89 °C (Found: C, 81·6; H, 6·1; MeO, 22·9%. Calc. for $C_{18}H_{16}O_2$: C, 81·8; H, 6·1; 2×MeO, 23·4%); light absorption in ethanol: $\lambda_{max.}$ (mμ) 341, 329, 300, *290*, 236; log $\varepsilon_{max.}$ 3·48, 3·48, 3·90, *3·86*, 4·78.

(*j*) *Dimethoxyphenylnaphthalenes from Haemocorin.* — The dimethoxyphenylnaphthalic anhydrides obtained by degradation of the aglycone ethers (Cooke and Segal 1955) were

decarboxylated in the first stage by mercuration and subsequent hydrolysis as described by Davies, Heilbron, and Irving (1932). The resulting monocarboxylic acids were further decarboxylated by heating with quinoline and copper chromite and the neutral products were purified as described above. The compound derived from the aglycone dimethyl ether A was identical (mixed m.p. and infra-red spectrum) with the 1,2-dimethoxy-6-phenylnaphthalene prepared as in (*h*) above (Found: C, 81·7; H, 6·4%. Calc. for $C_{18}H_{16}O_2$: C, 81·8; H, 6·1%). The material derived from the aglycone dimethyl ether B was identical (mixed m.p. and ultraviolet spectrum) with the synthetic 1,2-dimethoxy-8-phenylnaphthalene.

## V. Acknowledgments

Through the courtesy of Professor Sir Alexander Todd, F.R.S., some of this work was done at Cambridge (by R.G.C.). Travel grants from the British Council and from the Royal Society and Nuffield Foundation are also gratefully acknowledged.

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# EXTRACTIVES OF AUSTRALIAN TIMBERS*

## II. EMMOLIC ACID, A NEW TRITERPENE ACID FROM EMMENOSPERMUM ALPHITONIOIDES F.MUELL.

By J. P. Boyer,† R. A. Eade,† H. Locksley,† and J. J. H. Simes†

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*Summary*

Extraction of the wood of *Emmenospermum alphitonioides* F. Muell. yields a saponin, an essential oil, and a free triterpene acid, $C_{30}H_{46}O_5$, for which the name emmolic acid is proposed. Emmolic acid contains two hindered carboxyl groups, one double bond, and a secondary hydroxyl group which is located in a 5-membered ring in a β-position to one of the carboxyl groups. Chemical and spectroscopic evidence indicates that the double bond, which is easily reducible, is present in an *iso*propenyl group. Lactone formation involving interaction of a methoxycarbonyl group with the double bond occurs with dimethyl acetylemmolate and dimethyl emmonate. It is concluded that emmolic acid is probably pentacyclic with a carbon skeleton different from that of any of the naturally occurring triterpenes.

### I. Introduction

In the course of a survey of Australian flora for the occurrence of saponin, the leaves, wood, and bark of *Emmenospermum alphitonioides* F.Muell. gave indications of the presence of a saponin and also yielded crystalline, ether-soluble material which gave a positive Liebermann-Burchard test. Large-scale extractions of the wood with alcohol gave an amorphous, ether-insoluble saponin, a small quantity of a fragrant, steam-volatile oil, and a crystalline, ether-soluble substance which has been characterized as a new triterpene acid, $C_{30}H_{46}O_5$, emmolic acid. The quantities of saponin and emmolic acid in individual wood specimens varied considerably.

*E. alphitonioides*, commonly known as "bone wood", is a medium-sized tree indigenous to Australia and occurs sparsely in the forests of Queensland and northern New South Wales. It produces a hard, light coloured timber with a faint aromatic odour but is of little commercial value because of its comparative rarity. *E. alphitonioides* belongs to the family Rhamnaceae which is comparatively rich in saponin-containing plants (Webb 1948, p. 138: Tracey and Webb, personal communication 1957).

### II. Emmolic Acid

Emmolic acid was easily obtained pure by crystallization from methanol. Its homogeneity was demonstrated by chromatography of its dimethyl ester:

* For Part I of this series see *J. Chem. Soc.* **1950**: 2868.

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the original ester and each fraction had identical infra-red spectra ("Nujol")* and gave the same optical rotation. When the mother liquors from the crystallization of crude emmolic acid were treated with diazomethane and the product chromatographed, the only crystalline substance isolated was the same dimethyl ester; hence emmolic acid, unlike many triterpenes, does not appear to be accompanied by any significant amounts of related substances.

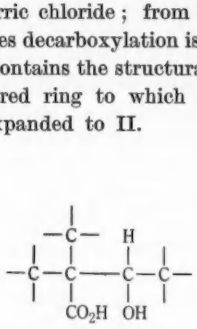
The low solubility of emmolic acid in most solvents made a determination of its molecular weight impracticable, but the more soluble dimethyl emmolate had an average value of 505; analyses of emmolic acid and its derivatives agree most closely with the formula $C_{30}H_{46}O_5$ for emmolic acid. Equivalent weight values of 248 and 249 were obtained by titration of an alcoholic solution of emmolic acid with aqueous alkali, and emmolic acid is consequently dibasic. Also, dimethyl emmolate, $C_{32}H_{50}O_5$, contains two methoxyl groups (Zeisel method) and in addition absorbed 1·04 moles hydrogen on catalytic hydrogenation to give dimethyl dihydroemmolate $C_{32}H_{52}O_5$. The possibility that emmolic acid has the formula $C_{31}H_{48}O_5$ cannot be entirely excluded particularly in view of the equivalent weight values.

Both carboxyl groups of emmolic acid are somewhat hindered as methylation by the Fischer-Speier method converted it only partly into the dimethyl ester; however, the dimethyl ester was formed quantitatively, using diazomethane. The hindered nature of the carboxyl groups was further evidenced by the difficulty of hydrolysis of the dimethyl ester which was virtually unaffected by heating under reflux for several hours with alcoholic potassium hydroxide. Lithium aluminium hydride readily reduced both methoxycarbonyl groups of dimethyl dihydroemmolate to the corresponding alcoholic groups.

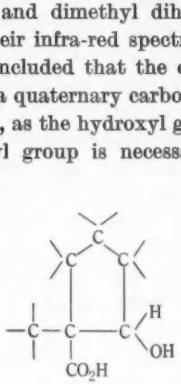
Acetylation of the hydroxyl group of emmolic acid was relatively difficult, but the product, acetylemmolic acid, was easily hydrolysed back to emmolic acid. Dimethyl emmolate was noticeably easier to acetylate than emmolic acid and it appears likely that hydrogen bonding between the hydroxyl group and one of the carboxyl groups is present in the free acid. Dimethyl dihydroemmolate gave the ketone, dimethyl dihydroemmonate, on oxidation with chromic anhydride-pyridine or in stronger conditions using chromic acid in acetic acid; dimethyl emmolate also gave the corresponding ketone, dimethyl emmonate, with chromic anhydride-pyridine. The keto group is very hindered and neither dimethyl dihydroemmonate nor dimethyl emmonate formed a 2,4-dinitrophenylhydrazone or an oxime even in forcing conditions. The presence of the keto group was evidenced by the characteristic weak absorption of both ketones near 302 mμ (ε, 50) which also shows that the keto group is not conjugated with the double bond or either of the methoxycarbonyl groups. The absorption at this comparatively long wavelength suggests that the keto group may be present in a 5-membered ring and this was confirmed by the infra-red spectrum of each ketone which had strong absorption at 1750 $cm^{-1}$. Obviously the original hydroxyl group is secondary.

* Except where otherwise indicated, all infra-red measurements were carried out in solution in carbon tetrachloride.

When emmolic acid was oxidized with chromic anhydride-pyridine, decarboxylation also occurred and the only product isolated was a ketomonocarboxylic acid. The ready decarboxylation of the presumed intermediate, emmonic acid, is ascribed to a β-relationship of the keto group and one of the carboxyl groups. Also, dimethyl emmonate and dimethyl dihydroemmonate do not show any evidence of enolization in their infra-red spectra and give no colour with ferric chloride; from this it is concluded that the carboxyl group which undergoes decarboxylation is present on a quaternary carbon atom. Thus emmolic acid contains the structural unit I and, as the hydroxyl group is present in a 5-membered ring to which the carboxyl group is necessarily attached, this can be expanded to II.



(I)



(II)

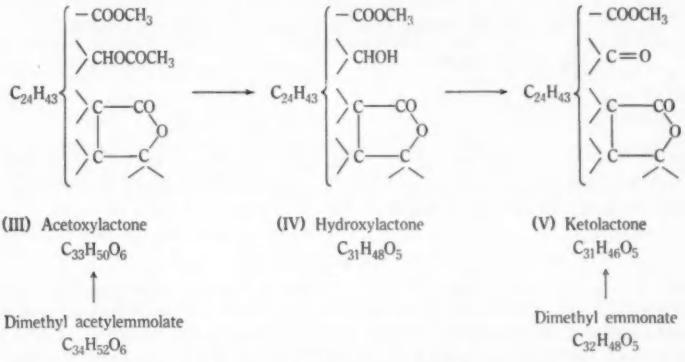
The presence of a double bond in dimethyl emmolate was indicated by the strong yellow colour given with tetranitromethane and by end-absorption in its ultraviolet spectrum. The double bond is quite reactive and dimethyl emmolate rapidly absorbed 1·04 moles of hydrogen on shaking with Adams catalyst in acetic acid. The saturated character of the product, dimethyl dihydroemmolate, was evidenced by its negative reaction with tetranitromethane and absence of end-absorption in its ultraviolet spectrum. Thus there is only the one double bond in emmolic acid which, based on the formula $C_{30}H_{46}O_5$,* must be pentacyclic.

The location of the double bond in a vinylidene group ($>C=CH_2$) was evidenced by the infra-red spectrum of dimethyl emmolate which had bands at 1642 and 888 $cm^{-1}$ ("Nujol"). The presence of the vinylidene group was confirmed by ozonolysis of dimethyl acetylemmolate which gave in one case 0·68 mole of formaldehyde isolated as the dimedone derivative and in a second case 0·41 mole of formaldehyde isolated as the 2,4-dinitrophenylhydrazone; the norketone produced had absorption at 1716 $cm^{-1}$ (shoulder) characteristic of a keto group in an open chain or 6-membered ring. The norketone also had absorption at 1355 $cm^{-1}$ corresponding to methyl bending adjacent to carbonyl (Cole 1954) indicating that it contains the group $-COCH_3$. In consequence the double bond of emmolic acid must be situated in an *iso*propenyl group. The norketone did not form either a 2,4-dinitrophenylhydrazone or an

* The analyses of emmolic acid and derivatives strongly favour the $C_{30}H_{46}O_5$ formula and consequently a pentacyclic structure has been selected for subsequent discussion; since this analytical evidence cannot rule out entirely the possibility of a formula such as $C_{30}H_{48}O_5$, other ring systems remain possible.

oxime and its lack of reactivity is reminiscent of that of the methyl ketone norlupanone (Jones and Meakins 1941).

Dimethyl acetylemmolate, $C_{34}H_{52}O_6$, when subjected to the same acidic conditions which effect the conversion of methyl betulonate into betulonic lactone (Davy, Halsall, and Jones 1951), gave a compound which was characterized as a γ-lactone by its absorption at 1780 $cm^{-1}$; it also had absorption at 1750 $cm^{-1}$ (acetoxy group) and 1733 $cm^{-1}$ (methoxycarbonyl group). The lactone ($C_{33}H_{50}O_6$, III) must have been formed by the interaction of the double bond and one of the methoxycarbonyl groups: it did not show any absorption in the infra-red ascribable to a double bond, gave no colour with tetranitromethane, and contained only one methoxyl group. On mild treatment with alkali (which did not affect the methoxycarbonyl and lactone groups) the acetoxylactone gave the corresponding hydroxylactone ($C_{31}H_{48}O_5$, IV) which




(III) Acetoxylactone $C_{33}H_{50}O_6$

(IV) Hydroxylactone $C_{31}H_{48}O_5$

(V) Ketolactone $C_{31}H_{46}O_5$

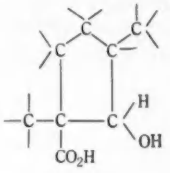
Dimethyl acetylemmolate $C_{34}H_{52}O_6$

Dimethyl emmonate $C_{32}H_{48}O_5$

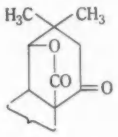
had absorption at 1780 $cm^{-1}$ (γ-lactone) and 1727 $cm^{-1}$ (methoxycarbonyl group). Oxidation of this gave the ketolactone ($C_{31}H_{46}O_5$, V) which was also obtained by the lactonization of dimethyl emmonate ($C_{32}H_{48}O_5$) in the same conditions as used with dimethyl acetylemmolate. The ketolactone had absorption at 1778 $cm^{-1}$ (γ-lactone), 1750 $cm^{-1}$ (keto group), and 1724 $cm^{-1}$ (methoxycarbonyl group). The absorption of the keto group at 1750 $cm^{-1}$ indicates that it is still present in a 5-membered ring system and hence it appears that this ring has not undergone expansion during the lactonization. The formation of the γ-lactone does not establish a definite relationship between the original position of the double bond and the carboxyl group concerned since the acidic conditions of the reaction could lead to double bond migration and skeletal rearrangements before lactonization occurred. Further studies are in progress concerning the identity of the carboxyl group involved in the lactonization.

The pentacyclic nature of emmolic acid and the presence of the *cyclo*pentane ring and the *iso*propenyl group suggest a relationship with the lupeol group, the only group of naturally occurring triterpenes possessing these features. However, dimethyl emmonate and dimethyl dihydroemmonate showed no absorption in

the infra-red between 1434 and 1395 $cm^{-1}$, indicating the absence of a methylene group adjacent to the carbonyl function in the *cyclo*pentane ring (Cole 1954). On this evidence the structural unit II in emmolic acid may be expanded to VI; thus the carbon skeleton of emmolic acid is different from that of lupeol and also from that of any of the naturally occurring triterpenes. The lactonization experiments also lend some support to this conclusion: it would be expected on analogy with the acid rearrangement of betulic acid that, if emmolic acid did in fact have the same carbon skeleton as lupeol, the ketolactone V would be of a type corresponding to VII in which the keto group is present in a 6-membered ring.




(VI)




(VII)

It is of interest that emmolic acid differs from most naturally occurring triterpenes which contain oxygen in that either it lacks the ubiquitous 3-oxygen function or else ring A is 5-membered.

## III. Experimental

Melting points are uncorrected. Ultraviolet spectra were determined in ethanol solution. Optical rotations were measured in chloroform using a 2 dm tube, except where otherwise stated. Methylations with diazomethane were effected by suspending or dissolving the material in ether containing 5–20% methanol and adding an excess of ethereal diazomethane at 0 °C; the reaction mixture was allowed to stand overnight at room temperature and then evaporated to dryness. The alumina used for chromatography was Peter Spence grade H. Neutralized alumina was prepared by washing grade H alumina with hot 2N nitric acid, then with water until the washings had pH 5·0, and finally with hot methanol; the alumina was reactivated by heating in a furnace at 450–500 °C for 8 hr. The light petroleum used in chromatographic separations had b.p. 60–80 °C.

Analyses are by Dr. E. Challen, N.S.W. University of Technology, and Dr. K. W. Zimmermann, C.S.I.R.O. Microanalytical Laboratory. Infra-red spectra were determined by Mr. I. Reece, N.S.W. University of Technology.

(*a*) *Preliminary Tests.*—A sample (5 g) of the finely ground wood of *E. alphitonioides* was extracted with boiling ethanol and the dried extract, which gave a brown colour in the Liebermann-Burchard test, was triturated with ether. The ether-insoluble fraction gave a brown Liebermann-Burchard test and was easily soluble in water giving a large froth stable for 2–3 days. The ether-soluble fraction was a brown resin which was insoluble in water but dissolved readily in hot methanol giving a mixture of colourless crystals and brown gum; it gave a reddish purple colour changing to brown in the Liebermann-Burchard test.

Samples of the bark and leaves of *E. alphitonioides* gave similar results.

(*b*) *Isolation of Emmolic Acid.*—The finely milled, dried wood (100 kg) of *E. alphitonioides* (from Tooloom State Forest, Casino, N.S.W.) was extracted with ethanol at room temperature; after three changes of solvent, when some 80 l. of ethanol had percolated through the sawdust, the extraction was virtually complete. The ethanolic solution was concentrated and poured

into ether; in practice, a 15 l. sample of the ethanolic extract was concentrated to 1 l. giving a brown syrup, quite mobile while warm (50 °C), which was then poured into ether (7 l.) with vigorous agitation. The resulting granular precipitate of crude saponin was triturated several times with ether, filtered, and dried (total yield 1·3 kg). The pale brown amorphous saponin readily dissolved in water giving a large durable froth on agitation and gave a brown Liebermann-Burchard test.

The ethereal-ethanolic solution was evaporated to dryness and the residue was exhaustively extracted with boiling light petroleum (b.p. 40–60 °C). Evaporation of the light petroleum gave a dark brown oil of weak but cloying odour, yield 39 g.

The light petroleum-insoluble residue dissolved readily in hot methanol giving a very dark brown solution which, after treatment with charcoal, deposited long, fibrous needles of *emmolic acid*. Concentration of the mother liquor yielded a gel which was readily filtered and which crystallized from methanol; this procedure was continued until no further gel could be obtained. The total yield of crystalline emmolic acid (m.p. 344–346 °C (decomp.)) was 30 g. Methylation of the residual concentrated mother liquors with diazomethane and purification of the product by chromatography on alumina gave dimethyl emmolate (m.p. 220–222 °C, yield 5 g) as the sole crystallizable product.

When the finely milled wood (7 kg) of a considerably older specimen of *E. alphitonioides* (obtained from northern Queensland) was subjected to the above extraction procedure, the yield of saponin was 230 g and of emmolic acid (m.p. 344–346 °C (decomp.)) 5·3 g.

(*c*) *Emmolic Acid.*—Emmolic acid crystallized from methanol in long, fluffy needles, m.p. 344–346 °C (decomp.), $[\alpha]_D^{28}$ +38° (*c*, 1·98; *l*, 1 in ethanol). Emmolic acid was moderately soluble in methanol and ethanol and virtually insoluble in chloroform, carbon tetrachloride, and light petroleum. It formed a sodium salt moderately soluble in water and only slightly soluble in ethanol; its equivalent weight was determined by titration of its solution in ethanol with aqueous sodium hydroxide. It gave a reddish purple colour slowly changing to brown in the Liebermann-Burchard test (Found: C, 73·9; H, 9·4; O, 16·6%; equiv. wt. 248, 249. Calc. for $C_{30}H_{46}O_5$: C, 74·0; H, 9·5; O, 16·5%; dibasic acid equiv. wt., 243).

(*d*) *Dimethyl Emmolate.*—(i) Emmolic acid (2 g) on methylation with diazomethane gave *dimethyl emmolate* which crystallized from methanol in heavy prisms (1·8 g), m.p. 223–224 °C, $[\alpha]_D^{28}$ +44·5° (*c*, 2·25; *l*, 1) (Found: C, 74·4; H, 9·7; $OCH_3$, 12·1%; mol. wt. (Rast), 502, 509. Calc. for $C_{32}H_{50}O_5$: C, 74·7; H, 9·8; $2\times OCH_3$, 12·1%; mol. wt., 515).

(ii) Emmolic acid (0·2 g) was dissolved in methanol (20 ml) and dry hydrogen chloride passed in for 1 hr at room temperature. The solution was then heated under reflux for 4 hr with continued passage of hydrogen chloride. It was allowed to stand overnight, concentrated to 5 ml, and poured into water. The resultant solid was shaken with an excess of cold aqueous 0·2N sodium hydroxide for 20 min and filtered. Acidification of the filtrate with hydrochloric acid produced a gel which crystallized from methanol in needles (0·05 g), m.p. 335–338 °C (decomp.), undepressed on admixture with authentic emmolic acid. The solid insoluble in aqueous sodium hydroxide was crystallized from aqueous ethanol and then methanol when it formed needles (0·05 g), m.p. 220–222 °C, undepressed on admixture with dimethyl emmolate prepared above.

(iii) *Homogeneity of Dimethyl Emmolate.* Dimethyl emmolate (m.p. 222–224 °C, 0·83 g) was dissolved in light petroleum-benzene (4 : 1, 125 ml) and chromatographed on alumina (2 by 28 cm). Elution with 1 l. each of light petroleum-benzene 4 : 1, 2 : 1, and 1 : 1 and benzene (1 l.) gave traces of material only; further elution with benzene (1 l.) gave fraction (1) (0·44 g), with benzene-chloroform (50 : 1; 1·5 l.) gave fraction (2) (0·22 g), with benzene-chloroform (20 : 1; 2 l.) gave fraction (3) (0·12 g), and finally with chloroform (0·5 l.) gave fraction (4) (0·03 g). Fractions (1), (2), and (3) were recrystallized (separately) from methanol forming heavy prisms in each case. Fraction (1) had m.p. 221–223 °C, $[\alpha]_D^{25}$ +45° (*c*, 1·79); fraction (2) had m.p. 220–222 °C, $[\alpha]_D^{25}$ +43° (*c*, 0·57); fraction (3) had m.p. 220–222 °C, $[\alpha]_D^{25}$ +45° (*c*, 0·34). Each of the three fractions showed no depression in m.p. on admixture with the original dimethyl emmolate and had identical infra-red spectra (paste in "Nujol").

(iv) *Attempted Hydrolysis of Dimethyl Emmolate.* A solution of dimethyl emmolate (0·1 g) in 10% ethanolic potassium hydroxide (10 ml) was heated under reflux for 2 hr. Water (40 ml) was added, the ethanol boiled off, and the mixture filtered. Acidification of the filtrate gave a small amount of gelatinous precipitate (0·002 g); the material precipitated by boiling off the alcohol was crystallized from methanol, forming prisms (0·085 g), m.p. 218–220 °C, undepressed on admixture with authentic dimethyl emmolate.

(*e*) *Dimethyl Acetylemmolate.*—A solution of dimethyl emmolate (1·3 g) in pyridine (5 ml) and acetic anhydride (5 ml) was heated on the steam-bath for 2 hr, cooled, and poured into water. The precipitate of *dimethyl acetylemmolate* crystallized from methanol in needles containing solvent of crystallization and after drying had m.p. 167–168 °C, $[\alpha]_D^{23}$ +28° (*c*, 2·88; *l*, 1), yield 1·1 g (Found: C, 73·2; H, 9·4; $OCH_3$, 11·1%. Calc. for $C_{34}H_{52}O_6$: C, 73·3; H, 9·4; $2\times OCH_3$, 11·1%). Dimethyl acetylemmolate sometimes crystallized from methanol in small plates, m.p. 158–159·5 °C.

(*f*) *Acetylation of Emmolic Acid.*—(i) Emmolic acid (3 g) was acetylated as in (*e*) and the dry amorphous product methylated with diazomethane. The methylated material was chromatographed on alumina (2 by 35 cm): elution with light petroleum-benzene (2 : 1, 3×500 ml) gave fraction (1) (1·55 g), fraction (2) (0·44 g) and fraction (3) (0·20 g); elution with benzene (1500 ml) and benzene-chloroform (6 : 1; 500 ml) gave traces of material only; further elution with benzene-chloroform (6 : 1; 1000 ml) gave fraction (4) (0·70 g); elution with chloroform (500 ml) and methanol (500 ml) gave small amounts of non-crystallizable gum. Fractions (1), (2), and (3) were recrystallized (separately) from methanol and each fraction had m.p. 166–167 °C, undepressed on admixture with the dimethyl acetylemmolate prepared in (*e*); the three fractions were combined and recrystallized from methanol (Found: C, 73·4; H, 9·3%). Fraction (4) was recrystallized from methanol when it had m.p. 220–222 °C, undepressed on admixture with authentic dimethyl emmolate (Found: C, 74·3; H, 9·8%).

(ii) A solution of emmolic acid (0·5 g) in pyridine (5 ml) and acetic anhydride (5 ml) was heated on the steam-bath for 3 hr, allowed to stand at room temperature for 24 hr, and then poured into ice-water. The product, which could not be crystallized, was dissolved in hot methanol from which, on cooling, it came down as a gel which was filtered and well washed with cold methanol. After five such purifications, the amorphous *acetylemmolic acid* (0·2 g) had m.p. 293–295 °C (decomp., softening at 288 °C), $[\alpha]_D^{25}$ +8·5° (*c*, 0·21; *l*, 1 in chloroform-ethanol, 4 : 1) (Found: C, 72·9; H, 9·3%. Calc. for $C_{32}H_{48}O_6$: C, 72·7; H, 9·2%).

(*g*) *Hydrolysis of Acetylemmolic Acid.*—Acetylemmolic acid (m.p. 293–295 °C (decomp.), 1·0 g) in 10% methanolic potassium hydroxide (50 ml) was heated under reflux for 2 hr, acidified with dilute hydrochloric acid and the resultant crystalline precipitate recrystallized from methanol when it formed needles (0·9 g), m.p. 338–340 °C (decomp.), undepressed on admixture with authentic emmolic acid. Methylation with diazomethane and recrystallization of the product from methanol gave prisms, m.p. 222–224 °C, undepressed when mixed with authentic dimethyl emmolate.

(*h*) *Reduction of Emmolic Acid.*—(i) *Dihydroemmolic Acid.* Emmolic acid (4 g) in acetic acid (300 ml) was catalytically hydrogenated (using Adams catalyst, 0·2 g) at room temperature when 199 ml of hydrogen (1·09 moles) was absorbed in 1 hr. After filtering off the catalyst, the solution was concentrated to 50 ml and poured into water; the product, which was difficult to crystallize, formed needles (methanol), m.p. 337–340 °C (decomp.), $[\alpha]_D^{20}$ +12° (*c*, 1·24 in ethanol) (Found: C, 73·6; H, 10·0%. Calc. for $C_{30}H_{48}O_5$: C, 73·7; H, 9·9%).

(ii) *Acetyldihydroemmolic Acid.* Acetylemmolic acid (m.p. 293–295 °C (decomp.); 2·7 g) was hydrogenated as above when 124 ml hydrogen (1·02 moles) was absorbed. The *acetyldihydroemmolic acid* could not be obtained crystalline; it was dissolved in hot aqueous ethanol from which it came down as a gel on cooling. After two such purifications the amorphous product had m.p. 301–303 °C (decomp.; softening at 298 °C), $[\alpha]_D^{25}$ —0·5° (*c*, 2·6 in chloroform-ethanol, 4 : 1) (Found: C, 72·8; H, 9·5%. Calc. for $C_{32}H_{50}O_6$: C, 72·4; H, 9·5%). The same product was also obtained by acetylation (pyridine and acetic anhydride) of dihydroemmolic acid.

(iii) *Dimethyl Dihydroemmolate.* Dimethyl emmolate (2·46 g) was hydrogenated as above when 109 ml of hydrogen (1·04 moles) was absorbed in 12 min and absorption then ceased. The *dimethyl dihydroemmolate* was crystallized from acetic acid and then from methanol from which it came down in heavy needles, m.p. 258–260 °C, $[\alpha]_D^{22}$ +22·5° (*c*, 1·8) (Found: C, 74·4; H, 10·1%. Calc. for $C_{32}H_{52}O_5$: C, 74·4; H, 10·1%).

(iv) *Dimethyl Acetyldihydroemmolate.* Acetylation of dimethyl dihydroemmolate with acetic anhydride in pyridine (2 hr on the steam-bath) gave *dimethyl acetyldihydroemmolate* which crystallized from methanol in needles containing solvent of crystallization; after drying, it had m.p. 155–156 °C, $[\alpha]_D^{25}$ +6·5° (*c*, 2·3) (Found: C, 73·4; H, 9·6%. Calc. for $C_{34}H_{54}O_6$: C, 73·1; H, 9·7%).

(*i*) *Dimethyl Dihydroemmonate.*—(i) A solution of chromic anhydride (0·5 g) in water (1 ml) and acetic acid (5 ml) was added over 30 min to a solution of dimethyl dihydroemmolate (0·5 g) in acetic acid (15 ml) maintained at 60–65 °C. The solution was kept at 60–65 °C for a further 1 hr and then poured into water. The precipitated *dimethyl dihydroemmonate* crystallized from methanol in needles (0·4 g), m.p. 191–193 °C, $[\alpha]_D^{25}$ +91° (*c*, 1·22), $\lambda_{max.}$ 302 mμ (ε, 47) (Found: C, 74·9; H, 9·8%. Calc. for $C_{32}H_{50}O_5$: C, 74·7; H, 9·8%).

(ii) A solution of dimethyl dihydroemmolate (1·12 g) in pyridine (15 ml) was added at 0 °C to the yellow slurry obtained by adding chromic anhydride (1·5 g) to pyridine (15 ml). The mixture was shaken vigorously, allowed to stand overnight at room temperature, and then poured into N hydrochloric acid (500 ml); sodium bisulphite (5 g) was added and the mixture extracted with ether. The ethereal extract, after washing with N sodium carbonate solution and water, yielded dimethyl dihydroemmonate which crystallized from methanol in needles (0·7 g), m.p. and mixed m.p. with (*i*) (i) above 191–193 °C, $[\alpha]_D^{20}$ +87° (*c*, 1·11) (Found: C, 75·0; H, 9·7%).

(*j*) *Dimethyl Emmonate.*—Dimethyl emmolate (0·27 g) was oxidized by chromic anhydride (0·3 g) in pyridine (3 ml) as in (*i*) (ii). *Dimethyl emmonate* was isolated from the diluted reaction mixture with ethyl acetate; it crystallized from methanol in fine needles (0·2 g), m.p. 161–163 °C, $[\alpha]_D^{23}$ +120° (*c*, 0·99), $\lambda_{max.}$ 303 mμ (ε, 51) (Found: C, 75·1; H, 9·6%. Calc. for $C_{32}H_{48}O_5$: C, 75·0; H, 9·4%).

(*k*) *Oxidation of Emmolic Acid.*—Emmolic acid (1 g) was oxidized by chromic anhydride (1 g) in pyridine (10 ml) as in (*i*) (ii). The product, on crystallization from methanol, gave *decarboxyemmonic acid* as needles (0·5 g), m.p. 252–254 °C (softening at 240 °C), $[\alpha]_D^{25}$ +92° (*c*, 0·93), $\lambda_{max.}$ 297 mμ (ε, 43). Its equivalent weight was determined by titration of its ethanolic solution with ethanolic potassium hydroxide (Found: C, 79·1; H, 10·2%; equiv. wt., 434. Calc. for $C_{29}H_{44}O_3$: C, 79·0; H, 10·1%; monobasic acid equiv. wt., 441).

With diazomethane, decarboxyemmonic acid gave the *methyl ester* which crystallized from methanol in needles, m.p. 122–124 °C, $[\alpha]_D^{23}$ +95° (*c*, 0·52) (Found: C, 79·5; H, 10·2; $OCH_3$, 6·9%. Calc. for $C_{30}H_{46}O_3$: C, 79·2; H, 10·2; 1×$OCH_3$, 6·8%).

(*l*) *Reduction of Dimethyl Dihydroemmolate with Lithium Aluminium Hydride.*—Lithium aluminium hydride (1 g) was added to a solution of dimethyl dihydroemmolate (0·7 g) in dry ether (40 ml) and the mixture heated under reflux for 8 hr. After standing at room temperature for 16 hr it was poured onto ice and 0·5N sulphuric acid (200 ml); some solid material separated at this stage and it was filtered off, washed with water, and combined with the residue obtained by evaporating the ethereal extract to dryness. Crystallized from methanol, the *triol* formed heavy prisms containing solvent of crystallization, m.p. 178–180 °C, with resolidification. After drying, the triol had m.p. 239–241 °C (yield 0·55 g), $[\alpha]_D^{30}$ +21·5° (*c*, 1·21 in chloroform-ethanol, 3 : 1) (Found: C, 78·3; H, 11·3%. Calc. for $C_{30}H_{52}O_3$: C, 78·2; H, 11·4%).

The triol was acetylated with acetic anhydride in pyridine (2·5 hr on the steam-bath) when it formed the *triacetate* which crystallized from methanol in prisms, m.p. 142–143 °C (yield 80%), $[\alpha]_D^{30}$ +3·5° (*c*, 1·98) (Found: C, 73·9; H, 9·8%. Calc. for $C_{36}H_{58}O_6$: C, 73·7; H, 10·0%).

(*m*) *Lactone Formation.*—(i) *The Acetoxylactone.* A solution of acetic acid (40 ml) and concentrated sulphuric acid (5 ml) was added to a solution of dimethyl acetylemmolate (0·5 g)

in benzene (5 ml) giving a clear, colourless solution. After standing for 6 days at room temperature, the now light purple solution was poured into water (400 ml) and extracted with benzene (4×50 ml). The benzene solution was washed with water, dilute aqueous sodium carbonate, and again with water; after drying, the benzene was removed and the crystalline residue recrystallized from methanol giving the *acetoxylactone* (0·36 g) in heavy prisms, m.p. 211·5–212·5 °C, $[\alpha]_D^{23}$ +69·5° (*c*, 0·86) (Found: C, 73·2; H, 9·3; $OCH_3$, 5·8%. Calc. for $C_{32}H_{50}O_6$: C, 73·0; H, 9·3; 1×$OCH_3$, 5·7%).

The same product was obtained (0·30 g from 0·50 g dimethyl acetylemmolate) when the reaction mixture was allowed to stand for 17 days at room temperature.

(ii) *The Hydroxylactone.* A solution of the acetoxylactone (0·3 g) in benzene (30 ml) was added to a solution of sodium methoxide (0·35 g) in methanol (7·5 ml) and the solution heated under reflux for 30 min. The reaction mixture was poured into an excess of dilute hydrochloric acid and the benzene layer washed twice with water, dried, and evaporated to dryness. The residue was dissolved in light petroleum-benzene (2:1; 30 ml) and chromatographed on neutralized alumina (16 by 1·5 cm): elution with light-petroleum benzene (2:1; 250 ml and 1:1; 250 ml) gave traces of material only; benzene (250 ml) gave fraction (1) (0·11 g, crystalline) and benzene-chloroform (9:1; 250 ml and 4:1; 250 ml) gave fraction (2) (0·11 g, crystalline); elution with chloroform gave uncrystallizable gum (0·03 g). Fractions (1) and (2) were recrystallized (separately) from light petroleum-benzene (4:1): fraction (1) formed needles, m.p. 258–260 °C, $[\alpha]_D^{23}$ +92° (*c*, 0·93); fraction (2) also formed needles, m.p. 258–260 °C (undepressed on mixing with fraction (1)), $[\alpha]_D^{23}$ +91° (*c*, 0·58). Fractions (1) and (2), constituting the *hydroxylactone*, were combined and recrystallized from light petroleum-benzene (4:1) to give needles, m.p. 258–260 °C (Found: C, 74·9; H, 9·7; $OCH_3$, 6·2%. Calc. for $C_{31}H_{48}O_5$: C, 74·4; H, 9·7; 1×$OCH_3$, 6·2%).

(iii) *The Ketolactone.* A solution of acetic acid (8 ml) and concentrated sulphuric acid (1 ml) was added to a solution of dimethyl emmonate (0·11 g) in benzene (1 ml) giving a clear colourless solution. The mixture was allowed to stand for 5 days at room temperature and the now light purple solution worked up as in (*m*) (i). The *ketolactone* (0·065 g) crystallized from methanol in needles, m.p. 220–222 °C (decomp.) (giving a sublimate of m.p. 320–325 °C (decomp.)), $[\alpha]_D^{24}$ +168° (*c*, 0·61), $\lambda_{max.}$ 302 mμ (ε, 42) (Found: C, 74·5; H, 9·4; $OCH_3$, 6·2%. Calc. for $C_{31}H_{46}O_5$: C, 74·7; H, 9·3; 1×$OCH_3$, 6·2%).

When a sample of the reaction mixture was allowed to stand 15 days, the product had m.p. and mixed m.p. identical with the product isolated after 5 days.

A solution of chromic anhydride (0·05 g) in water (0·1 ml) and acetic acid (2 ml) was added over 1 hr to a solution of the hydroxylactone (0·08 g) in acetic acid (3 ml) at 40 °C. The reaction mixture was then heated for 1 hr at 60 °C, poured into water, and extracted with ether. The ether layer was washed with water, dilute aqueous sodium carbonate and water, dried, and the ether evaporated. The residue crystallized from methanol in needles (0·06 g), m.p., and mixed m.p. with the ketolactone prepared above, 220–222 °C (decomp.) (giving a sublimate m.p. 320–325 °C (decomp.)), $[\alpha]_D^{23}$ +165° (*c*, 0·54) (Found: C, 74·7; H, 9·3; $OCH_3$, 6·2%). The infra-red spectra (paste in "Nujol") of the ketolactone prepared by the two methods were identical.

(*n*) *Ozonolysis of Dimethyl Acetylemmolate.*—(i) A stream of ozonized oxygen was passed through a solution of dimethyl acetylemmolate (1 g) in methylene chloride (200 ml) at −10 to −15 °C for 1·5 hr when the solution had become saturated with ozone. After the mixture had come to room temperature, acetic acid (15 ml) was added and zinc dust (4 g) added over 30 min to the vigorously stirred mixture. The mixture was stirred for a further 45 min, filtered, and the filtrate extracted with water (6×30 ml). The aqueous extract was adjusted to pH 7 (sodium bicarbonate) and saturated aqueous dimedone solution (70 ml) added. On standing in the refrigerator for 12 hr, this deposited the dimedone derivative of formaldehyde which after recrystallization had m.p. and mixed m.p. with an authentic specimen 186·5–187·5 °C, yield 0·32 g (68%) (Found: C, 69·9; H, 8·4%. Calc. for $C_{17}H_{24}O_4$: C, 69·8; H, 8·3%). Evaporation of the dried methylene chloride solution gave crystalline material (0·8 g) which was purified

by chromatography on alumina when three major fractions (0·11, 0·16, and 0·18 g) were obtained. On recrystallization from methanol (prisms) these all had m.p. and mixed m.p. 240–243 °C and the fractions were combined. The *norketone* had $[\alpha]_D^{23}$ +0·5° (*c*, 0·74), $\lambda_{max.}$ 279 mμ (ε, 30) (Found: C, 70·9; H, 8·9%. Calc. for $C_{32}H_{30}O_7$: C, 70·9; H, 9·0%).

(ii) In a further experiment, dimethyl acetylemmolate (3 g) in chloroform (300 ml) was ozonized at —20 °C and the decomposition of the ozonide was carried out as in (*n*) (i). The neutralized aqueous solution was distilled and the formaldehyde isolated as the 2,4-dinitrophenylhydrazone (0·46 g, 41%) in the usual way. The recrystallized formaldehyde 2,4-dinitrophenylhydrazone had m.p. and mixed m.p. with an authentic specimen 166 °C (Found: C, 40·1; H, 2·6; N, 26·7%. Calc. for $C_7H_6O_4N_4$: C, 40·0; H, 2·9; N, 26·7%). The dried chloroform solution was evaporated to dryness and the crystalline residue of norketone was recrystallized from methanol when it formed heavy prisms (2 g), m.p. 240–243 °C, $[\alpha]_D^{20}$ —2° (*c*, 1·31) (Found: C, 70·9; H, 9·3%).

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# SHORT COMMUNICATIONS

## THE SYNTHESIS OF 4–CHLORO–2–[$^{14}$C]METHYLPHENOXYACETIC ACID (" METHOXONE ")*

By A. M. Downes† and K. R. Lynn‡

In recent years 4-chloro-2-methylphenoxyacetic acid (" Methoxone ") has become an accepted selective herbicide. As part of a study of the translocation and metabolism of this compound in plants a sample labelled in the methyl group with $^{14}$C was required by our colleague, Mr. C. G. Greenham.§ The synthesis from barium [$^{14}$C]carbonate is described here. " Methoxone " does not appear to have been labelled with $^{14}$C previously, but Sorensen (1951) labelled the compound with $^{36}$Cl for use in isotope dilution analysis.

Some of the 4-chloro-2-[$^{14}$C]methylphenoxyacetic acid has been tested on bean plants. Although a small amount of the radioactive carbon (less than 1 per cent.) is converted to carbon dioxide, the labelled compound is suitable for a number of investigations. The work is continuing (Greenham, personal communication).

[$^{14}$C]Carbon dioxide was converted to [*carboxy*-$^{14}$C]salicylic acid by the Kolbe reaction using a procedure similar to that of Mandel and Smith (1950). The salicylic acid was reduced by lithium aluminium hydride to *o*-hydroxy-[*alcoholic*-$^{14}$C]benzyl alcohol which was further reduced by Raney alloy to yield [*Me*-$^{14}$C]*o*-cresol (Papa, Schwenk, and Whitman 1942). Neither of these intermediates was isolated. The *o*-cresol was converted directly to *o*-[$^{14}$C]methylphenoxyacetic acid by reaction with chloroacetic acid. Chlorination of this compound in glacial acetic acid at 100 °C (Sorensen 1951) gave the crude product which was purified by paper chromatography. The overall yield of the pure " Methoxone " from barium carbonate was about 10 per cent. However, as only one radioactive run was performed this yield could probably be improved. Although the chlorination reaction produced only 36 per cent. of the product, the unchlorinated acid was recovered and could be used again.

*Experimental*

The radiochemical yield at each stage was determined by carrier dilution analysis. All samples were counted at infinite thickness in polythene disks (Popják and Beeckmans 1950) with a thin end-window Geiger-Mueller tube. Melting points are uncorrected.

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[Carboxy-$^{14}$C]*salicylic Acid.*—Freshly cut sodium (73·7 mg) was dissolved in dry ethanol (2 ml) in a glass tube (about 20 by 1·3 cm) with a constriction near the open end. A solution of phenol (314 mg) in ethanol (1 ml) was then added and the solution evaporated to dryness in a stream of nitrogen. The tube was attached to a vacuum manifold (Calvin *et al.* 1949) and evacuated to less than $10^{-3}$ mm Hg for several hours to remove the last traces of ethanol. Carbon dioxide (1 mMole; 790 μc; generated from $Ba^{14}CO_3$ obtained from the Radiochemical Centre, Amersham, England) was then condensed into the tube by means of liquid oxygen and the tube sealed off *in vacuo*. The tube was allowed to warm to room temperature and was then heated at 140 °C for 20 hr inside a steel container. After cooling to room temperature, the contents of the tube were dissolved in water, acidified, and extracted with ether. The ethereal solution was extracted with aqueous sodium bicarbonate. Acidification of the aqueous extract yielded crude [*carboxy*-$^{14}$C]salicylic acid (yield 135·6 mg, 98 per cent. based on $BaCO_3$; 785 μc/mMole), m.p. 150–156 °C. Paper chromatography of this material in *n*-butanol-5N ammonium hydroxide indicated that the salicylic acid was contaminated with approximately 1·5 per cent. *p*-hydroxybenzoic acid. The crude salicylic acid was recrystallized from water (121 mg), m.p. 158–159 °C (lit. 159 °C). [*Carboxy*-$^{14}$C]salicylic acid was prepared in this way several times in connection with other work, the yield of the recrystallized product never being less than 70 per cent. A portion of this high specific activity material was diluted with carrier for the subsequent reactions.

2-[$^{14}$C]*Methylphenoxyacetic Acid.*—An ethereal solution of [*carboxy*-$^{14}$C]-salicylic acid (181 mg; 161 μc; 123 μc/mMole) was treated with lithium aluminium hydride (Brown 1951) to yield *o*-hydroxy[*alcoholic*-$^{14}$C]benzyl alcohol as an extract in 10 per cent. aqueous sodium hydroxide. This extract was treated with Raney alloy according to the method of Papa, Schwenk, and Whitman (1942). The resulting alkaline solution of [*Me*-$^{14}$C]*o*-cresol (radiochemical yield 70·0 μc, 44 per cent.) was converted directly to 2-[$^{14}$C]methylphenoxyacetic acid (62 mg, 28 per cent. based on $BaCO_3$; 118 μc/mMole), m.p. 152 °C (lit. 152 °C) by reaction with chloroacetic acid.

*4-Chloro-2-*[$^{14}$C]*methylphenoxyacetic Acid.*—Chlorine (5 per cent. in excess of the theoretical amount) was generated by the method of Brown, Gillies, and Stevens (1953) and carried in a stream of $N_2$ into a solution of 2-[$^{14}$C]methylphenoxyacetic acid (62 mg) in glacial acetic acid (25 ml). The crude product was chromatographed on four sheets (20 by 45 cm) of Whatman No. 3 MM paper, using *iso*amyl alcohol-5N ammonium hydroxide as the solvent. Autoradiography (with "Kodirex" film) of the developed chromatograms revealed the presence of two radioactive bands, one ($R_F$ 0·33) corresponding to unchanged starting material and the other ($R_F$ 0·57) to the product. The "Methoxone" bands were eluted with water and the aqueous solution decolorized with charcoal, filtered, and finally freeze-dried to yield "Methoxone" as the ammonium salt (yield 29·4 mg, 10·3 per cent. based on $BaCO_3$; 120 μc/mMole). The product was found to be at least 99 per cent. radiochemically pure when examined by chromatographic techniques and by carrier dilution analysis.

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## EXAMINATION OF *INTSIA* (*AFZELIA*) *BIJUGA* BARK*

By W. Korytnyk†

*Intsia bijuga* (Leguminosae) is a commercial timber also known as Cairns teak in Queensland. It also occurs in New Guinea and is probably identical with the commercial timber kwila. Its sawdust and bark have been found to be devoid of alkaloids (Dr. H. J. Rodda, personal communication). The bark has now been examined for neutral and acid constituents and was found to contain 0·37 per cent. of β-amyrin and 0·10 per cent. of a saturated fatty acid material having the properties of the "cerotic" acid mentioned in Beilstein.

### *Experimental*

Analyses were carried out by the C.S.I.R.O. Microanalytical Laboratory.

4·5 kg of ground bark (collected at Clump Point, Queensland, during 1951) was percolated with cold light petroleum (b.p. 40 °C) and yielded an oily green residue *A*. Subsequent percolation with cold methanol gave a dark brown residue *B*.

Residue *A* was shaken with light petroleum (b.p. 40 °C) and filtered. The solid residue was dissolved in benzene and adsorbed on an alumina column. The major fraction was eluted by chloroform and when recrystallized from ethyl acetate yielded 3·5 g of β-amyrin, m.p. 197–198 °C, $[\alpha]_D^{18}$ 88·9° (*c*, 1·1 in chloroform) (Found: C, 84·3; H, 11·9%. Calc. for $C_{30}H_{50}O$: C, 84·4; H, 11·8%). Its infra-red spectrum in carbon tetrachloride solution was very similar to the published spectrum for β-amyrin (Allsop *et al.* 1956). The acetate prepared by reaction with acetic anhydride and pyridine had m.p. 237–238 °C, $[\alpha]_D^{18}$ 81·5° (*c*, 0·9 in chloroform) (Found: C, 81·75; H, 11·2%. Calc. for $C_{32}H_{52}O_2$: C, 82·0; H, 11·2%). Mixed m.p. with authentic β-amyrenyl acetate (kindly supplied by the Division of Industrial Chemistry, C.S.I.R.O., Melbourne) was undepressed and the infra-red spectra of the two specimens ("Nujol" mull) were identical. White (1956) records for β-amyrin, m.p. 199·5–200 °C, $[\alpha]_D$ 88° and its acetate, m.p. 241 °C, $[\alpha]_D$ 81°.

Residue *B* was suspended in water and extracted with chloroform. This extract was shaken with aqueous sodium hydroxide, when a considerable amount of water-insoluble sodium salt was formed. The neutral chloroform-extract was chromatographed as described above, and yielded another 13·1 g of β-amyrin.

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The sodium hydroxide-extract was filtered and the insoluble sodium salt was obtained as a partial gel. After washing with water, it was dissolved in hot ethanol, treated with charcoal, and filtered while hot. The free acid was precipitated by the addition of dilute hydrochloric acid.

The dried acid (4·6 g) was converted to its methyl ester by means of diazomethane, dissolved in light petroleum (b.p. 40–60 °C) and carefully chromatographed on an alumina column. The major fraction was eluted by benzene light petroleum (1 : 10) and, after being recrystallized from methanol the waxy plates had m.p. 61–62 °C. The infra-red spectrum in carbon tetrachloride solution was typical of an ester of a saturated fatty acid and was characterized by a triplet absorption at 8·0, 8·33, and 8·51 μ (Shreve *et al.* 1950) (Found: C, 78·8; H, 13·2%. Calc. for $C_{27}H_{54}O_2$: C, 79·0; H, 13·3%). Methyl ester of "cerotic" acid is recorded as having m.p. 60 or 62 °C (Beilstein). Hydrolysis of the ester by methanolic sodium hydroxide yielded the acid, which was recrystallized several times in methanol and light petroleum to a constant m.p. of 78–79 °C (Found: C, 78·6; H, 13·2%. Calc. for $C_{26}H_{52}O_2$: C, 78·7; H, 13·2%). Various workers (Beilstein) report the m.p. of "cerotic" acid, a mixture of straight chain saturated carboxylic acids, in the range 77·5–79 °C.

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*References*

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## Corrigendum

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Page 5, the last sentence should read: The integrated count rate is then treated as if it were uniformly distributed over the capillary length and multiplied by the integral or $\bar{r}$ as under,

$$\int_0^l c(x)\mathrm{d}x \int_0^l \bar{r}(x)\mathrm{d}x = I_u. \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

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